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TRANSLITERATION

There is no ideal system of translit-
erating Russian, each has its advantages
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Geokhimiya we have chosen the system
used by *Chemical Abstracts*, partly be-
cause of its wide acceptance by other
journals and partly because of certain
advantages in alphabetization of names.
The principal differences between this
system and others in common use are as
follows:

Russian	Chem. Abs.	Others
X	kh	h
И	ts	tz
III	shch	sch
Ю	yu	iu
Я	ya	ia

THE ISOTOPIC COMPOSITION OF ADMIXTURES OF LEAD IN ORES AND MINERALS AS INDICATION OF THEIR ORIGIN AND OF TIME OF THEIR FORMATION

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Abstract

The isotopic composition of lead impurities in various nonlead ores (pyrite, coprite, sphalerite, copper-pyrrhotite, tungsten, copper-nickel ores a.o.) can be used as an indicator to show similarities in their genesis and contemporaneity of their formation. This has been shown for various deposits of the Kola and Kalba as well as the copper-nickel deposits of Norilsk and the Kola Peninsula. The isotopic composition of the lead impurities of cassiterites is also valuable. A comparison of data for the areas studied shows the importance of geological factors in the origin of the isotopic composition of ore lead.

I. INTRODUCTION

We have been calling attention repeatedly to the fact that the isotopic composition of lead impurities in any ore may be used as the means of identifying the ore-forming processes and of determining the time of their concurrency in time [1, 2, 3].

We know that the total lead in rocks is not a homogeneous and uniformly distributed isotopic mixture, inasmuch as every one of the rock-forming minerals has its own specific isotopic lead composition. The fractionation of lead from the rock, however (i.e. the separation of lead from its parent elements), results in isotopic homogenization. The resulting mixture of lead isotopes finds its way into ores and minerals, and it is the isotopic composition of this lead that is diagnostic of a particular ore-forming process.

There is no possibility of fractionation of lead isotopes during the formation of the ore, not to any appreciable extent, regardless of whether the lead assumes the form of an independent mineral or whether it enters some other mineral as an impurity. The only process, therefore, that could disturb the isotopic ratios in such lead would be mixing with lead from some other source.

We hope eventually to return to the principles of the mixing of lead in ore-forming processes and, consequently, to the interpretation of anomalies in the isotopic composition of lead. The topic of the present article is the stability of the isotopic composition of lead, not in galena

or in other lead minerals, but in ores and minerals of different kinds formed synchronously in one and the same ore deposit or over more extensive areas.

In this connection we examined a series of pyrite-polymetallic and metal ores from several ore deposits in Rudnyi Altai and Kalba, as well as some copper-nickel ores from Norilsk and the Kola Peninsula. We examined discrete sulfide minerals (chalcopyrite, pyrite, pyrrhotite, sphalerite, galena), fine-grained and medium-grained sulfide ores of different composition, as well as quartz, scheelite, wolframite, and cassiterite. With the exception of galena, the lead content of most of them was 0.01 to 0.0005%, and lower.

II. METHODS

The chemical method used in the extraction of lead from sulfide minerals involved their decomposition with acid followed by electrolysis. Extremely small quantities of lead were extracted by dithionite. Pyrochemical methods were used in the case of scheelite, wolframite, cassiterite, and quartz. Single-mineral aliquots were ignited at 1300°C. for 4 to 10 hours in a stream of hydrogen, whereupon the residual deposit of the sublimated metal in the cooled part of the receptacle was dissolved in 5% HNO_3 . The solution was transferred onto a watch glass and evaporated to dryness. In the case of very small quantities of lead (up to 30 micrograms), purified copper nitrate was added as the carrier. Under such conditions, 5 to 10 gram aliquots of the sample were used. The analysis was performed by the mass-spectrographic procedure with the use of the hot anode and the zirconium-silicate emitter [4].

III. MATERIALS

Deposits of the Rudnyi Altai (polymetallic and pyrite-polymetallic) and of the Gornyi Altai and Kalba (the rare-metal type) belong to the late-Harz metallogenic stage. At the Rudnyi Altai-Kalba boundary, the folded zone of the Irtysh, there are several groups of pyrite-polymetallic, copper, and copper-pyrrhotite deposits. Among them the Berezovskoe and the Novo-Berezovskoe belong to the first type. M. S. Bezsmertnaya [5] differentiates several stages of ore formation in these latter deposits. The specimens we had examined (Table 1) are representative of all of the stages except the late polymetallic one. Sample No. 1 represents pyrite-magnetite veinlets—the ore belonging to the earliest oxide-sulfide stage of the mineralization. The next stage, the sulfur-pyritic, is represented by samples of massive pyrite (Nos. 3, 4). The sulfur-pyritic stage is followed by the copper-pyrrhotite stage. Both of these parageneses are joined in Sample No. 5 in which the bulk of the early pyrite is replaced by a fine-grained pyrrhotite aggregate with small amounts of chalcopyrite and

Table 1. Isotopic Composition of Lead from Ores of Rudnyi Altai*

Source	Sample	Isotopic Ratios		
		Pb ²⁰⁶ /Pb ²⁰⁴	Pb ²⁰⁷ /Pb ²⁰⁴	Pb ²⁰⁸ /Pb ²⁰⁴
Berezovskoe	Veinlets of pyrite with magnetite	17.89	15.67	37.98
Berezovskoe	Veinlets of pyrrhotite with galena	17.83	15.58	37.77
Novo-Berezovskoe	Pyrite ore	17.89	15.60	37.80
Novo-Berezovskoe	Pyrite ore	17.86	15.62	37.87
Novo-Berezovskoe	Pyrite-pyrrhotite ore	17.86	15.66	37.80
Novo-Berezovskoe	Copper-pyrrhotite ore	17.89	15.60	37.88
Novo-Berezovskoe	Sphalerite ore	17.92	15.60	37.75
Novo-Berezovskoe	Sphalerite ore with galena	17.92	15.61	37.82
Chudak	Sphalerite with chalcopyrite	17.86	15.52	37.67
Bukhtarminskoe	Chalcopyrite-pyrite ore	17.83	15.49	37.56
Vavilonskoe**	Chalcopyrite-pyrrhotite ore	17.86	15.48	37.64
Vavilonskoe	Pyrrhotite ore	17.89	15.56	37.70
Berezovskoe	GALENA	17.76	15.57	37.70
Belousovskoe	Pyritic ore with sphalerite and chalcopyrite admixture	18.02	15.71	37.98
Belousovskoe	Chalcopyritic ore with sphalerite and admixture of galena	18.08	15.62	37.99
Belousovskoe	Pyritic ore with chalcopyrite, sphalerite, and galena	17.92	15.63	37.97
Belousovskoe	Pyritic ore with chalcopyrite, sphalerite, and galena	17.95	15.65	38.02
Belousovskoe	Pyritic-polymetallic ore	18.05	15.73	38.07
Belousovskoe	Pyritic-polymetallic ore	18.05	15.73	38.02
Belousovskoe	GALENA, coarse-grained	17.99	15.66	38.05
Zyryanovskoe	Disseminated polymetallic ore	17.78	15.39	37.60
Zyryanovskoe	Fine-grained polymetallic ore	17.76	15.34	37.35
Zyryanovskoe	"Dull ore"† from quartz vein	17.76	15.47	37.63
Zyryanovskoe	Chalcopyrite	17.80	15.49	37.70
Zyryanovskoe	GALENA	17.87	15.44	37.79
Zyryanovskoe	Fine-grained polymetallic ore	17.92	15.53	37.40
Zyryanovskoe	GALENA	17.85	15.54	37.50

* Isolated from all samples by chemical procedures.

† Authors are deeply grateful to T. V. Zorova for having placed these samples at their disposal.
 ** "Dull ore" is translated as "dull ore"; the term applies to sulfides of variable composition, e.g. (Zn, Fe, Cu)₂(As, Sb)₄S₁₃ commonly with admixtures of Hg, Ag, Pb, Ni, Co, Bi, etc. VPS.

lerite. The copper-pyrrhotite stage as such is expressed in sample No. 6—a massive fine-grained pyrrhotite ore with small quantities of chalcopyrite. No galena could be detected in polished sections at 10X magnifications in Samples 1 to 5. The preponderantly sphalerite ores with chalcopyrite and pyrrhotite (No. 7) and with a little galena (No. 8) constitute varieties of the subsequent polymetallic stage. Veinlets of pyrrhotite-galena ores (No. 2) also belong to the same stage, together with the galena of the polymetallic ore (No. 13). All of these samples were selected from different ore bodies of the Berezovskoe and the Novo-Berezovskoe deposits at different depths and in different tectonic environments. Moreover they represent the entire sequence of magmatic complexes throughout the ore-depositing process. The Belousovskoe deposit also belongs to the pyrite-polymetallic stage. Its ores consist either of 80% pyrite with some sphalerite and admixtures of chalcopyrite and galena (Nos. 14, 16, 17) or represent the polymetallic type in its proper sense, with large proportions of pyrite, sphalerite, and galena (Nos. 18, 19). Here too some almost pure chalcopyrite ores may be found locally (with galena as scarce

isolated grains smaller than 0.01 mm in diameter), as in No. 15, as well as coarsely-crystalline galena (No. 20).

The Chudak copper deposit, not far from the Berezovskoe, is represented by Sample No. 9—sphalerite ore with some chalcopyrite. The composition of lead extracted from this material is identical with the isotopic composition of the Bukhtarminskoe copper ores (No. 10) 100 km southeast of the Chudak and with the composition of the lead ores from the copper-pyrrhotite Vavilonskoe deposit (Nos. 11 and 12) 40 km west of the Chudak. The Vavilonskoe ores contain insignificant admixtures of syngenetic galena [6].

The Zyryanovskoe deposit, already in the control part of the Rudnyi Altai, belongs to the polymetallic type. Samples of disseminated polymetallic ores (No. 21), fine-grained polymetallic ores (No. 22), and galena from veinlets cutting the fine-grained ores (No. 25) were taken from one part of this deposit, together with a sample of the "dull ore" from an isolated quartz vein (No. 23). These samples represent all of the most common ore types of this deposit (the dull ore is relatively rare).

Chalcopyrite (No. 24) is typical of the copper ores in the Pravoberezhovskii section of the Zyryanovskoe, where the polymetallic ores have only minor expressions. Two additional samples, the fine-grained massive ores (No. 26) and galena from quartz-carbonate veinlets (with coarse-grained sulfides) cutting through the fine-grained ores (No. 27) were taken from a different flank of the same deposit.

The rare metal deposits of Kalba and Gornyi Altai are in the zones adjoining the polymetallic and the pyrite-polymetallic mineralized zones of the Rudnyi Altai. In this case, the ores are associated with quartz veins carrying a tin-wolframite mineralization in the Kalba and a molybdenum-wolframite one in the Gornyi Altai.

Samples from the stockwork deposit at Cherdoyak in the Kalba-Narym district (Table 2) are represented by scheelite (No. 29), quartz

Table 2. Isotopic Composition of Lead from Kalba-Narym District*

Sample No.	Deposit	Mineral	Isotopic Composition		
			Pb ²⁰⁶ /Pb ²⁰⁴	Pb ²⁰⁷ /Pb ²⁰⁴	Pb ²⁰⁸ /Pb ²⁰⁴
28	Cherdoyak	Quartz	17.99	15.65	37.77
29	Cherdoyak	Scheelite	17.95	15.64	37.94
30	Cherdoyak	Cassiterite	24.45	15.86	37.78
31	Leninskoe	Cassiterite	24.69	15.56	37.57
32	Leninskoe	Cassiterite	21.03	15.40	37.66
33	Chalche**	Cassiterite	29.94	15.99	37.54
34	Chudskoe	Quartz	17.92	15.58	37.69
35	Karash	Wolframite	18.03	15.40	37.55
36	Skalistoe	Quartz	18.05	15.68	37.89

*Lead was isolated by the pyrochemical method.

**Sample supplied by V. L. Barsukov (GEOKhI).

o. 28), and cassiterite (No. 30) from one and the same section of the rockwork. Composition of the lead from cassiterite is definitely anomalous: the content of Pb^{206} is very high. The leads from cassiterites and two other similar deposits in the same district, the Leninskoe and the Chalche (Nos. 31 and 32 respectively) show the same kind of anomalies in their isotopic composition, but a different intensity. The possible causes of such anomalies will be treated later in the discussion. In addition to the samples here enumerated, we examined also quartz from Chudskoe (No. 34), wolframite from Karash (No. 35)—both from the quartz-cassiterite formation—and a quartz from the Skalistoe deposit belonging to the quartz-tourmaline-wolframite type (No. 36). As stated, an abundant molybdenum mineralization and a complete absence of cassiterite are typical of the rare metal belt of the Gornyi Altai, i.e., the reverse of the Kalba pattern. As in the case of the Erdoyak, we examined the lead from quartz (No. 37) and from wolframite (No. 38), both from a vein of the Chernovinskoe deposit, and also from the wolframites of the Ekipetskoe quartz vein deposit (No. 39) belonging to the neighboring Turgusun group of rare metal ores (Table 3).

Table 3. Isotopic Composition of Lead from Gornyi Altai*

Sample No.	Deposit	Mineral	Isotopic Composition		
			Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}
7	Chernovinskoe	Quartz	18.02	15.58	37.70
8	Chernovinskoe	Wolframite	17.95	15.61	37.87
9	Ekipetskoe**	Wolframite	18.05	15.69	37.97

*Lead was isolated by the pyrochemical method.

**Sample supplied by O. M. Chirko to whom the authors are greatly indebted.

The next districts whose ores were examined in the present study are the Norilsk and the Kola Peninsula. Galena is a mineralogical peculiarity in these districts, in spite of their entirely sulfide character. There is one such specimen of galena ore from Norilsk. Lead is present nevertheless in the ores of these districts to the extent of thousandths and ten-thousandths of one per cent. Lead can be used accordingly as an indicator of ore-forming processes. The copper-nickel sulfide ores are related genetically to intrusions of basic and ultrabasic rocks. In the Norilsk district, they are related to the differentiated gabbro-diabase intrusions of different composition, classified as early Mesozoic Traprock Formation; in the Monche-Tundra, to differentiated Proterozoic intrusions of pyroxenites. There are basic and ultrabasic intrusions also in the Pechega district: gabbros, pyroxenites, serpentinites. These deposits were regarded formerly to be of the magmatic-liquational type. In recent years, however, a

hydrothermal origin has been suggested for the Pechenga and for some of Monche-Tundra ores [8].

Table 4. Isotopic Composition of Lead from Northern Siberia*

Sample No.	Source	Material	Geologic Age	Pb ²⁰⁶ /Pb ²⁰⁴	Pb ²⁰⁷ /Pb ²⁰⁴	Pb ²⁰⁸ /Pb ²⁰⁴	Au/thorite
40	Norilsk	Chalcopyrite	Lower Mesozoic	17.81	15.24	37.54	[2]
41	Norilsk	Platinum	Lower Mesozoic	17.90	15.29	37.53	[2]
42	Norilsk	Galena	Lower Mesozoic	17.88	15.27	37.50	[7]
43	Taimyr	Galena in carbonate veinlets in traprock	Lower Mesozoic	17.99	15.25	37.50	[7]
44	Taimyr, Shumilikha	Galena	Lower Mesozoic	17.92	15.35	37.60	
45	Podkamennaya Tunguska	Galena from ore in Silurian limestone	Lower Mesozoic	17.97	15.35	37.72	[7]
46	Podkamennaya Tunguska, Glin-yanyi Klyuck	Galena	?	18.87	15.40	37.75	

*Lead extracted by the chemical method.

The isotopic composition of lead from chalcopyrite (No. 40), platinum (No. 41), and galena (No. 42) from one and the same deposit is entirely the same (Table 4). Characteristically, galenas from different places in the north of Central Siberia have practically the same isotopic composition of lead [7] which is analogous to the isotopic composition of lead in the ores of Norilsk, as in Sample Nos. 43, 44, and 45. This analogy has led to the supposition that all of these ores are related genetically to the Trap Formation [7]. We should note nevertheless that there are also galenas in Central Siberia which are evidently of other origins. Thus the lead from galena in the same area of the Podkamennaya Tunguska District (No. 46) contains somewhat more Pb²⁰⁸ than the other samples of lead here enumerated.

In the case of the copper-nickel ores of the Kola Peninsula, we examined the lead (Table 5) from massive chalcopyrite-pyrrhotite (No. 47) and pyrrhotite (No. 48) of the Nittis-Kumuzhe deposit, as well as from samples of three different ores of the Pechenga district (Nos. 49, 50, 51). No galena could be detected microscopically in any one of these five samples.

IV. DISCUSSION AND TENTATIVE CONCLUSIONS

The lead isolated from pyritic, pyrrhotitic, sphaleritic, copper-pyrrhotitic, chalcopyritic, and other ores of the Berezovskoe, Belousovskoe, and Zyryanovskoe deposits in the Rudnyi Altai proved to be

practically the same, isotopically, in every one of these deposits and essentially the same as the lead isolated from their galenas. The isotopic composition of lead from the first three of them is very similar indeed. The lead from the Bukhtarminskoe, Chudak, and Vavilonskoe of the Berezovskoe type. The lead from the Zyryanovskoe [2] deviates appreciably from the type, showing, moreover, a much wider range of variation in its isotopic composition.

The leads from quartz, wolframite, and scheelite of the rare metal deposits of the Kalba and of the Gornyi Altai are likewise identical isotopically, with the exception of the lead from the Kalba-Narym cassiterites. The latter is anomalous because of its high Pb^{206} . The greatest anomaly is observed in the case of cassiterite from the Chalche, in which there is not only the maximum of Pb^{206} but also a definite increase in Pb^{207} ; this is never the case for the other cassiterites. Such isotopic anomalies originated evidently after the deposition of the ores and are related, in the cassiterites, to the presence of disseminated radioactive minerals of some kind. Considering the young age of the mineralization, about 250 million years, the post-ore accessions of Pb^{207} must have been rather insignificant.

According to N. K. Morozenko [9], cassiterites from the Kalba quartz vein deposits contain 0.07 to 0.85% $(Ta,Nb)_2O_5$, whereas a cassiterite from a pegmatite contains up to 1.65% $(Ta,Nb)_2O_5$. The average of 7 analyses is 0.42% for cassiterites of the first type. At the same time, there are only traces of the sum of tantalum and niobium pentoxides in the wolframites; in one case their sum is only 0.09%. M. F. Melkin [10] reports only very small quantities of the pentoxides in the

Table 5. Isotopic Composition of Lead from Kola Peninsula*

Sample No.	Source	Material	Geologic Age	Isotopic Composition		
				Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}
7	Monche-Tundra**	Massive chalcopyrite-pyrrhotite ore	Proterozoic	16.86	15.29	36.07
3	Monche-Tundra	Massive pyrrhotite ore with pentlandite	Proterozoic	16.78	15.20	36.05
9	Pechenga †	Pyrrhotite ore	Proterozoic or Ordovician?	15.22	14.85	34.50
10	Pechenga	Massive pyrrhotite ore	Proterozoic or Ordovician?	15.27	14.89	34.38
	Pechenga	Pyrrhotite-pentlandite ore	Proterozoic or Ordovician?	15.17	14.79	34.57

* Lead extracted by the chemical method.

** Specimens from the collections of the A. E. Fersman Memorial Institute of Mineralogy, Academy of Sciences of the USSR.

† Specimens placed at our disposal by O. E. Yushko-Zakharova to whom the authors are greatly indebted.

two light-brown cassiterites from the Cherdoyak (less than 0.05% to traces). The presence of tantalum and niobium is characteristic of the dark varieties of cassiterite, nevertheless, and it is the dark varieties of cassiterite that constitute our samples.

We are led, therefore, to the supposition that our cassiterites contain some columbite. Uranium is present in cassiterite, as a rule, and this fact may explain the isotopic anomalies in the lead. The lead in cassiterite may be represented accordingly by two types: the ordinary one, dispersed in the cassiterite crystal structures, and the radiogenic lead in the accessory columbites, zircons, and other uraniferous minerals.

It follows from the foregoing discussion that even small admixtures of uranium or thorium may be responsible for isotopic anomalies in the small quantities of lead present in the given mineral. Not all of the isotopic anomalies need be related to the deposition of the ore. However, comparisons of the isotopic data on lead from quartz, scheelite, and wolframite allow us to maintain that the lead in these minerals may be a reliable indicator both of the time and of the process by which the ores were formed.

The isotopic composition of lead in the ores from Central Siberia, specifically, from Norilsk, Taimyr, the Nizhnyaya and the Podkamennaya Tunguskas, is practically the same and resembles in some instances the isotopic composition of lead in some ores of the Altai.

In comparing the tables, we should observe that Pb^{206} and Pb^{208} in the somewhat younger Norilsk ores are the same as in the Altai ores. On the other hand, Pb^{207} is appreciably lower in the Norilsk ores than in the pyrite-polymetallic and the copper-pyrrhotite ores of the Altai; their Pb^{207} corresponds to the lowest levels of this isotope in the Zyryanovskoe ores [2], Altai.

The similar isotopic ratios in the lead from the Altai and the Central Siberian ores may be due to their genetic relationships respectively to magmas of the granitoid series (with their high U/Pb and U/Th ratios) and to the basic magmas (the Trap Formation). The specific geochemical features of different districts are expressed therefore in the isotopic ratios of their lead, which must be taken into account in comparisons between the isotopic characteristics of the lead in different provinces. The same community of genetic relationships with the basic and ultrabasic rocks may be indicated by the similarity of the Pb^{207} values in the Norilsk and the Monche-Tundra ores, so different in their geologic age.

Curiously, the Pechenga ores, whose lead has the same isotopic composition, proved to be much older than the lead in the Monche Tundra-Nittis Kumuzhe ores. The Pechenga lead is most likely to be Lower Proterozoic. Although many geologists do regard the Pechenga mineralization as Lower Proterozoic, there are still opinions to the effect that it is Caledonian, of the same age as its host rocks—the Pechenga-Kuchin Suite, as stated, for example, in the latest summary

of geology of the Murmansk Area [11]. This latter opinion is not sustained by the data on the isotopic composition of the lead.

The age of lead is definitely indicated by its isotopic composition in materials from the Kola Peninsula and indeed throughout the entire Fennoscandia. Also, even within a given range of variation of the age of origins of the ores, the Identity Rule for the isotopic composition of lead impurities in different ores is still effective. We shall discuss this subject in detail in our next paper.

In the meanwhile, we may draw the following tentative conclusions from the data here reported.

There can be no doubt whatsoever that the so very similar, not to say identical, isotopic compositions of lead in different minerals from one and the same ore body or from different ore bodies in one and the same mineralized belt, as well as in different rare-metal mineralized belts at some distance from each other (the Kalba and the Gornyi Altai) are single-value indicators of their genetic unity and of their contemporaneous origin. The genetic unity needs be understood apparently either as a unity of the source of the ores or as two sources of lead, identical in their geochemical characteristics, with the further understanding that these alternatives apply also to the other constituents of the ore substance (tin, tungsten, molybdenum). If all of these elements were borrowed from some other source (host rocks, etc.) than the source of the lead, there would be a simultaneous borrowing of lead of some other isotopic composition. If we consider the commonly small quantities of lead in minerals of the rare-metal veins, any addition of foreign and not entirely magmatic lead would result inevitably in a displacement of the isotopic ratios of the lead, in either direction. Under such conditions we would have obtained an isotopic pattern of the type observed in polymetallic deposits of the Rudnyi Altai [2], in which there is an appreciable scattering of the isotopic ratios of the lead in different deposits (Zyryanovskoe, Leninogorskoe, etc.).

These relationships enable us to make use of the isotopic composition of lead admixtures as an aid in the identification of the ore-forming process for any kind of ore, that is, they enable us to consider the community of origin and the synchronism of deposition not only of lead ores but also of polymetallic ores on the basis of the isotopic composition of their lead.

Comparisons between the isotopic analyses of lead from the Altai and from the Central-Siberian North demonstrate the importance of the geologic factor in the evolution of the isotopic composition of lead. The geologic factor is absolutely indispensable in any generalizations dealing with origin and the age.

The isotopic analyses of lead from the Monche-Tundra ores sustain their Proterozoic age, whereas they indicate a still more ancient age of the Pechenga ores, probably Lower Proterozoic. A Caledonian age of the Pechenga ores and, accordingly, of their host rocks (the Pechenga-Kuchin Suite) does not agree with the results of the isotopic analyses of their lead. This problem requires more thorough investigation.

We have demonstrated that the isotopic composition of lead from cassiterites is anomalous. This shows that minerals in which admixtures of accessory radioactive minerals may be expected are not suited for genetic and age analysis. At the same time, however, anomalies of the kind we had established in cassiterites may give us some information on the specific geochemical and physico-chemical environments at the time of the deposition of the ores. For example, the relatively high-temperature cassiterites are generally richer in the admixtures and may be that much more anomalous accordingly. If so, we have an additional criterion for the identification of pegmatitic, pneumatolytic-hydrothermal, and hydrothermal types of cassiterites.

In conclusion, the authors give their deepest thanks to E. B. Evdokimova, who had carried out all of the time-consuming work involved in the chemical and the pyrochemical preparation of the samples for the mass-spectrographic analysis.

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PROBLEMS OF PETROGENESIS IN THE
LIGHT OF EXPERIMENTAL DATA*N. I. Khitarov*V. I. Vernadskii Memorial Institute of Geochemistry and
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Abstract

On the basis of experimental data resulting from experiments carried out at high T and P, as well as from the analysis of some peculiarities of volcanic eruptions, a series of genetic problems has been deciphered. It is concluded that most water, being isolated during the eruption of basaltic magma, must be related to the erupting of basaltic magma itself. The basaltic magma is the least altered primary magmatic substrate.

Furthermore the general process of the formation of rocks of a pure line has been considered as a process of successive transformation of the basic magma. This process occurs chiefly during the crystallization period, on account of the variation in the system H_2 -Fe- H_2O ; water being the chief regulating agent in the process.

Upon direct acquaintance with the magnificent manifestations of modern volcanism, one becomes keenly aware of the limitations of our knowledge of a whole series of problems involving general ideas on geologic processes, including the problem of origin of igneous rocks.

Only recently, the Bezmyannyi volcano, one of the Klyuchevskaya group in the Kamchatka, showed an entirely exceptionally effective display of volcanic activity. According to G. S. Gorshkov's description [1], the eruption began in October 1955 but attained its critical stage only in March 1956. At that time, after several months of preparation consisting of a gradual expansion of the central part of the volcanic center, there was a tremendous explosion—a powerful expulsion of substance, with the formation of a cloud of gas and ash and a subsequent outpouring of lava. The cloud was more than 40 kilometers (132,000 ft) high. Up to 24.5 kilograms ash per m^2 (5 lb per sq ft) fell in the vicinity of the Volcanologic Station of the Academy of Sciences at the Klyuchevskaya Settlement. The energy of the explosive wave was estimated at 5×10^{22} ergs by G. S. Gorshkov. Gigantic bodies of the ash and the powerful explosive effect suggest a measure of participation of volatile substances in the eruption and, above all, of water.

The author became acquainted with the activities of the Bezmyannyi volcano in the Kamchatka several months after the explosion. The field evidence has led to many questions. It was in connection with the availability of certain new experimental findings, pertinent to some field

problems, that the present article was begun, in the form of a general discussion.

The phenomenon of the expansion of the volcanic center has raised an important question regarding the physical state of the conduit-center. The observed inflation of the dome was indicative not merely of colossal pressures owing to the intruding magma but also of a hermetic sealing of the main conduit walls at relatively great depths. It is for these reasons that the accumulated pressure was discharged not laterally but upwards along the main conduit. A phenomenon of this sort, that is, the focusing of the subterranean forces and their emergence at the surface only through a restricted area (the cross-section of the outlet), despite their tremendous potential energy, even if we make allowances for the availability of the secondary channels, tells us something about the specific environment in the main conduit channel.

Deep-seated tectonic disturbances, in the course of a very long time, with occasional interruptions, are functioning as sources of materials of a relatively uniform type, with only minor differences in composition, as a rule. Such relative uniformity of composition suggests a single source of the materials and also a certain constancy in the environments traversed by magmatic solution in its ascent from the depths to the surface.

Tectonic phenomena at depth must cause a rapid definite ascent of the magma, under dynamic tensions, at the same time as its solid burden is undergoing disruption. Under such conditions, the first parts of the ascending magma, as they pass through consolidated bodies of host rocks, must be used up as inner linings of the conducting channel, with the resulting thermal insulation of the channel, minimizing thereby any possibility of changes in the composition of the advancing magmatic solution by interaction with its environment.

Judging by our experimental findings, viscosity of a basaltic melt, for example, is relatively high at 900°C and 2000 kg/cm² water vapor pressure. If so, this high viscosity, conducive to the insulation of the channel, must become manifest from great depths upwards, at the time when the first portion of the ascending magma is passing through the tectonic cavity.

After extinction of activity of the volcanic apparatus, the conducting channel is plugged as a rule. Depending on local conditions, this plugging may be deep or shallow. The general regime of the accessions of magma to the conducting channel and of the exchanges of heat between the channel and surrounding rocks are the definitive factors in the life of the channel. The extensive and common phenomenon of recurrent disruptions through the old channel and through one and the same outlet to the surface is indicative both of adequate accessions of heat to the channel itself and of the prolonged conservation of heat inside the channel.

The time of re-activation of the volcanic apparatus is determined by variation in its geologic environment as a whole. Moreover, the

re-activation requires a repeated warming-up, made effective by means of a resumption of active contacts between the more or less cooled upper sections of the channel and its hot sections at deeper levels of the magmatic column. Transfers of heat, in this case, take place not only by convection in the magmatic solution as a whole, but also to a significant extent by means of hot volatile constituents ascending to the upper parts of the column. Physical state of the magmatic solution, under the circumstances, is determined mainly by three parameters: temperature, pressure, and chemical composition of the melt, as well as of the co-existing volatile phase.

Viscosity must also be taken into account in silicate melts, such as magmas, as one of the principal characteristics determining properties of magmatic solutions. Viscosity determines also the possibilities of the attainment of uniformity in the composition of a magmatic solution and, conversely, the possibilities of variations in its composition.

The phenomena of temperature gradients caused by increasing pressures in the system, with the resulting powerful convection currents of heat, are well known experimentally. We also have had some experience with such phenomena in the fields of high pressures. Not so long ago, Vereshchagin and Kalashnikov [2] investigated them experimentally and analyzed them theoretically, by means of an inquiry into the character of thermal fields in gaseous media in the presence of free convection, on the premises of Grashof and Prandtl. The analysis shows that, in relation to variations in the density of gas, as influenced by pressure, there are variations in the density of the thermal flow, in its changes from a laminar to a turbulent movement. Transfers of heat increase abruptly on increasing convection. When the autoclave is heated internally, the increasing convection, in a gaseous medium under pressure, causes a drop in the temperature of the central part of the autoclave (Fig. 1). The upper part of the cavity proves to be hotter than the middle. Thus, according to Vereshchagin and Kalashnikov [2], the following indications were obtained, in their experiments with Ar, N_2 , H_2 (Table 1).

Temperature differences between the center and the top of the autoclave, in argon or nitrogen media, may be up to 50% of temperature of the center. In contrast with other gases, hydrogen media show but an insignificant difference, although even there $\pm 12^\circ C$

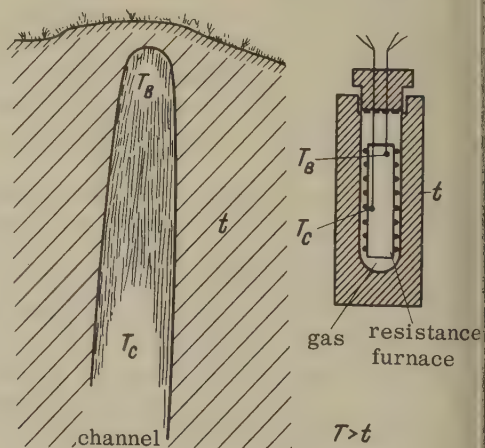


Fig. 1.

Table 1

Gas	Pressure, atm.	Temperature, top, °C	Temperature, middle, °C	ΔT, °C
Ar	1	575	584	-9
Ar	520	535	358	+177
N ₂	1	524	569	-45
N ₂	540	333	224	+109
N ₂	1000	308	219	+89
H ₂	1	328	347	-19
H ₂	600	203	231	-28

variations, in different parts of the autoclave, are observed even at the pressures of 600 atm. This difference in the behavior of hydrogen may be explained by its low viscosity and its high thermal conductivity, which is 7 to 12 times as high as the conductivity, e.g., of argon or of nitrogen.

Effects of hydrogen on the thermal regime are clearly illustrated by Basset's findings, in his experiments with a resistance furnace placed in a high-pressure autoclave filled with hydrogen [3]. Power consumption increases markedly with increasing pressures, in this particular case. The power required for the maintenance of the temperature at 500°C, in nitrogen and hydrogen media, is reported in Table 2. The increasing consumption of the current by the furnace at increasing pressures is indicative of a powerful transport of heat by hydrogen resulting from the convection.

Phenomena taking place in internally heated apparatus, as examples, approximate to some extent a general picture of relationships operating in a magmatic channel in the present discussion. Although the data here cited refer to gases, the phenomenon as such is observable also in liquid media and may be extended to include also gas-bearing magmatic solutions.

The role of volatile substances in the break-through at the surface consists not only of the cumulative dynamic effort but also in their current chemical interaction with rocks of the overburden, involving even a penetration by liquefaction, whereby the resistance of the rock is lowered significantly. A combination of these two effects may lead, in some cases, to piercing of the overburden by gas without any

Table 2

Gas	Pressure, Kilograms per cm ²						
	1	500	1000	2000	3000	5000	6000
Nitrogen	44	82	110	145	165	192	200
Hydrogen	54	143	183	235	265	308	325

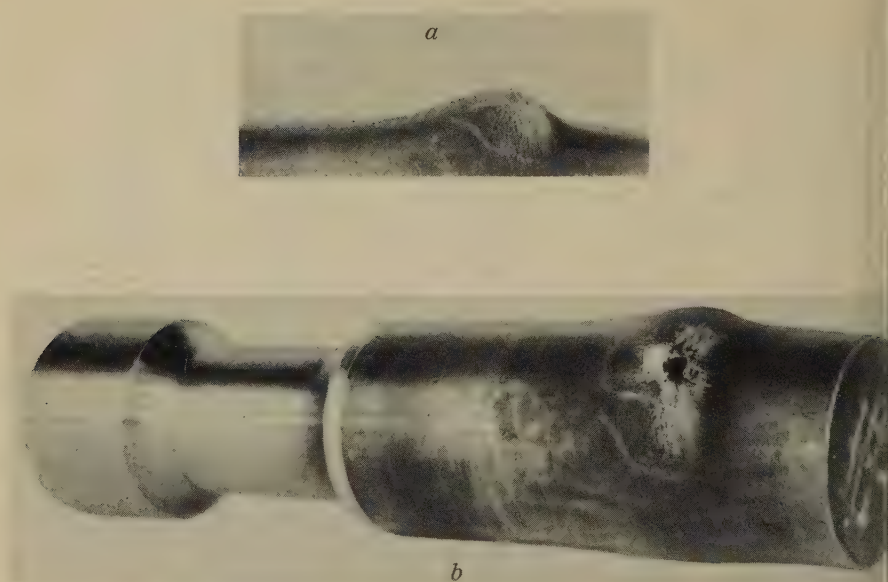


Fig. 2. High Pressure Autoclave: a—the inflated section, side view; b—the rupture, top view.

appreciable bulging of the lid. Examples of this sort may be recognized in the morphology of some parasitic cones of the Klyuchevskoi volcano and in the descriptions of their developments. An example resembling somewhat the rupture by the gases has developed in one of our experiments with powdered albite and water in a steel autoclave. Some time after the temperature inside the autoclave rose to 760°C , at 3000 atm. pressure, there was an explosion of the autoclave, with the formation of a typical crater funnel in its weakly bulged wall (Fig. 2).

Gaseous constituents entering the upper part of the magmatic column do not cause any substantial alteration of magmatic materials, since they are at a relative equilibrium with the magmatic solution. A confirmation of this view may be found in the data on chemical composition of many lavas and volcanic ashes, simultaneously formed, as for example in the Bezymyanni volcano (according to Gorshkov, Table 3).

The rapid ascent of the magma and its insulation from the surrounding rocks result in a conservation of $\text{H}_2 - \text{H}_2\text{O}$, the main regulators of the magmatic process, while preserving and controlling chemical and physical characteristics of the magma.

The gas, as we know, is an important regulator of properties of the melt, and the gas responds quickly to any change in the pressure. Consequently, many variations in composition of the melt are

contingent on distribution of the
as. Environmental variations in
the bulk of the magmatic sub-
stratum as a whole must be oper-
ating continuously therefore, on
this or that scale, depending on
circumstances, and their influence
on the progress of the magmatic
process must become manifest
with the dimension of time.

$H_2 - H_2O$ and, to some extent,
 O_2 are the principal carriers
of heat, among the volatile sub-
stances. Their gradual accumu-
lation in the conduit channel is
accompanied by a build-up of

the pressure to the point where it overcomes the external resistance
and is relieved by a volcanic explosion.

The fact of the accumulation of volatile substances is supported by
many observations in regard to resumptions of activities in different
volcanic apparatuses accompanied by eruption phenomena, expulsion
of ash, and release of large quantities of volcanic substances.

Effects of oxidizing environments conducive to shifting the equilib-
rium in favor of water may be expected only in the uppermost part of

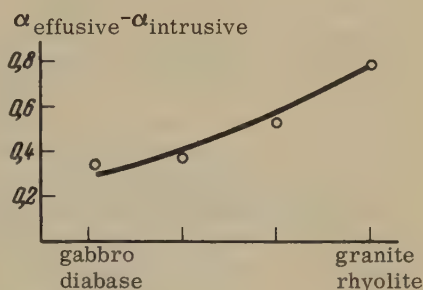


Fig. 3

Table 3

Constituent	Bezmyyanni Volcano		Apakhonchich Lava
	Ash %	Lava of hornblende andesite %	Olivine Basalt %
SiO ₂	59.79	59.48	50.10
TiO ₂	0.89	0.65	1.03
Al ₂ O ₃	17.39	17.59	19.99
Fe ₂ O ₃	3.79	4.08	4.19
FeO	3.15	2.93	5.02
MnO	0.12	0.14	0.25
CaO	7.16	6.82	8.58
MgO	2.82	2.49	5.98
Na ₂ O	3.67	3.66	2.84
K ₂ O	1.27	1.29	1.52
H ₂ O ⁻	0.25	0.10	0.21
H ₂ O ⁺	0.29	0.77	0.21
Sum	100.59	100.00	99.81

Note: The ash fall during the eruption and the first portion of the horn-
blende andesite lava are nearly identical. The main difference is
in the preponderance of Fe^{+++} over Fe^{++} in the lava.

the channel. It is under such conditions that we have accessions of basic magma to the surface. The low viscosity of basaltic magma, its high fluidity and the resulting high rate of its ascent, the insulation of the ascending materials from the enclosing works—these are the factors that make it possible for *basic basaltic magma* to appear at the surface.

The same factors serve as the most rational justification of our view to the effect that *basaltic magma represents the original magmatic substratum least affected by alterations*. Assuming that basic magma is the parent magma, we must consider now, first of all, some fundamental variations in the environments of the magmatic process, despite the crudity of our approximations.

The First Case to be discussed is when the parent basaltic material comes into direct contact with the surface of the ground, on account of deep-seated progressive tectonic disturbances; as, for example, in the instance of effusions through major fissures, in platform terrains, the case in question has the following characteristics:

- a) The contact between the magmatic hearth and the surface of the ground is relatively well-sustained.
- b) Reactions between the magma and its environment are limited.
- c) The partial pressure of H_2 is relatively high.

These characteristics are markedly different from those of the *Second Extreme Case* which is most likely to be effective in folded terrains, when:

- a) The emergence of basaltic lava at the surface is impeded.
- b) Tectonic disturbances are numerous and are varied in their types and location, conducive to developments of fractured zones in the upper and in the intermediate tectonic tiers, if not in the deeper ones.
- c) Reactions between the magma and its environment are facilitated and are conducive to assimilation.
- d) The partial pressure of H_2 is falling off, and the role of water, the principal donor of oxygen, is increasing concurrently.

If we consider the analytical averages of Daly [4] of the chemical composition of igneous rocks, we conclude that the $Fe_2O_3:FeO$ ratio (α) and the participation of oxygen in the stabilization of the rock increase progressively from basic to acidic rocks both in the effusive and intrusive series (Table 4).

The increase of α toward the acidic end of the series indicates oxidizing environments and shifts of the equilibria in favor of water, and the necessity of taking these factors into consideration with reference to equilibria in the system as a whole.

If we take into account also the decrease of $\Delta\alpha = \alpha_{\text{eff.}} - \alpha_{\text{intr.}}$ toward the basic members of the series (Fig. 3), it develops first that the role of water is equally important both in the effusive and in the intrusive facies of the magmatic process, under certain definite conditions and, second, that both effusive and intrusive series have a certain community in the principle of their evolution from the basic to the acidic rocks.

Table 4

Constituent	Rock							
	Gabbro	Diorite	Grano-diorite	Granite	Basalt	Andesite	Dacite	Rhyolite
SiO ₂	48.24	56.77	65.01	70.18	49.00	59.59	65.68	72.80
Fe ₂ O ₃	3.16	3.16	1.74	1.57	5.38	3.33	2.38	1.45
FeO	5.95	4.40	2.65	1.78	6.37	3.13	1.90	0.88
α _{int.} *	0.53	0.72	0.66	0.80	-	-	-	-
α _{ef.} *	-	-	-	-	0.84	1.10	1.20	1.66

int. and α_{ef.} are Fe₂O₃:FeO ratios in the intrusive and the effusive rocks respectively.
PS.

Let us turn now to the experimental data, from the newer point of view, which serves further to clarify the role of water in the formation of rocks. The data on reactions between basalt and water are particularly interesting in this connection. As test material we used olivine basalt from the lava flow of a parasite cone of the Klyuchevskoy volcano known as the Apakhonchich and described by S. I. Naboko [5], who has kindly placed samples at our disposal. This basalt is an abundantly distributed product of parasite cones of the Klyuchevskoy that has developed in the past 20 years. It is a dark rock with microlites of clinoclase, pyroxene, and kernels of an ore mineral in a brown-yellow glassy matrix. The phenocrysts are plagioclase diopside-augite and olivine. Chemical analysis of the rock is reported in Table 3. The interaction of basalt with water was brought about in a horizontal reactor placed inside an oven at predetermined temperature and

Table 5*

Constituent	Apakhonchich basalt	T = 450°C; P = 600 atm; 140 hrs		Mariupolite nepheline syenite
		Initial 20 hrs	Terminal 40 hrs	
	1	2	3	4
SiO ₂	57.4	96.0	61.5	60.0
Al ₂ O ₃	22.9	2.3	26.0	21.2
Fe ₂ O ₃	4.9	0.4	1.6	2.4
CaO	9.8	0.1	0.5	1.2
Na ₂ O	3.3	0.4	9.4	11.6
K ₂ O	1.7	0.8	1.0	3.6
Sum	100.0	100.0	100.0	100.0

Analyses for the oxides are re-calculated to make the sum 100%.
Note: 1 - analysis of the original basalt;
2 and 3 - composition of mineral substance in the condensate, after 20 and 40 hours of interaction between water and basalt; T. N. Kozintseva, Analyst.
4 - from Zhdanov District; E. A. Kuznetsov, "Petrografiya Magmatischenkikh i Metamorficheskikh Porod" ("Petrography of Magmatic and Metamorphic Rocks"). NGU (the Government University of Moscow), 1956.

pressure. The water passed through the cavity of the reactor, at a constant rate, reacting with a basalt layer (3 to 5 mm deep), and through a cooler where it was collected, as a condensate, for chemical analysis. The first series of the tests was performed at 450°C and 600 atm., with a continuous passage of the water for 140 hrs (Table 5).

Under the experimental conditions, beginning with the very first hours of the interaction, as the water was percolating through the reactor cavity containing the basalt, we noted a weak acidity in the solution accompanied by an increase in silica up to 96%. The other constituents of the rock were present in the solution in definitely subordinate quantities. As the reaction between basalt and water continued, the amount of silica passing into solution tapered off. There was a concurrent increase in dissolved alumina, sodium, a smaller increase in dissolved potassium and iron, and a still smaller one in calcium. Practically no magnesium could be detected, despite its abundance in the original rock.

In a series of experiments under more drastic conditions, at 600°C and 3000 atm., the phenomenon of the solution of silica-rich constituents becomes even more emphatically manifest. Here too interactions with water result, first of all, in a separation of solutions rich in silica. The SiO_2 content is up to 96% in the first fractions of the condensate. The silica content decreases with time, during the water-rock interactions, while the contents of alumina and sodium, primarily, and of potassium and calcium and iron, to a lesser degree, increase progressively. Magnesium remains practically unaffected.

The microscopically visible changes are about the same in all of the experiments. The fundamental alterations consist merely of a dissolution of the glass and of a degradation of the matrix with its microlites. Consequently the glassy part of the rock is represented by acid materials and easily leached out of the rock upon its interaction with water. The residual part of the rock becomes enriched concurrently with these constituents characterizing the more basic rock varieties: magnesium, calcium, and iron.

Analysis of the leached-out substance shows that, at 450°C and 600 atm., the interaction of basalt with water leads in the beginning to the separation of silica-rich fractions which pass into solution toward the end of the experiment (during 140 hours), and that the composition of the dissolved mineral substance is very close to the composition of nepheline syenites of the mariupolite type. Under more drastic conditions, at 600°C and 3000 atm., the contact of basalt with water leads to the separation of mineral solutes corresponding to rhyolite in their composition. This fraction is yielded by basalt after 2 to 3 hours of interaction. After 15 hours of the interaction, the dissolved substance comes to resemble keratophyre in its composition (Table 6).

Consequently, if prior to an effusion of basaltic lava, some supplementary water of extraneous origin were to make its appearance, and this were not in equilibrium with the advancing lava, there would be a change in the composition of the lava, and its original basaltic aspect would not be preserved.

Table 6

Constituent	Apakhonchich basalt	T = 600°C; P = 3000 atm.; 15 hrs				
		Initial 2 hours	Next 2 to 3 hours	Liparite from Karadag, Crimea	Terminal 5 hours	Quartz keratophyre, Mt. Magnitnaya
	1	2	3	4	5	6
SiO ₂	57.4	92.4	79.74	79.96	75.3	77.1
Al ₂ O ₃	22.9	5.0	10.73	11.54	16.7	13.5
Fe ₂ O ₃	4.9	trace	0.11	0.60	0.1	0.7
CaO	9.8	0.2	0.21	1.22	0.2	0.5
MgO	3.3	1.1	5.38	4.15	6.3	5.8
K ₂ O	1.7	1.3	3.83	2.53	1.4	2.4
Sum	100.0	100.0	100.0	100.0	100.0	100.0

1 - the original basalt.

2, 3, and 5 - mineral substance in the condensate after the indicated period of interaction of water with basalt; E. E. Filippova, Analyst.

4 - from E. A. Kuznetsov, op. cit. in note to Table 5.

6 - from V. I. Luchitskii, "Petrographiya," T. 2, 1932.

There is no established opinion regarding the origin of water released by volcanic eruptions. We do not know whether this water is magmatic, juvenile, or whether it is partially or entirely unrelated to the magmatic hearth. *By the foregoing consideration, with basaltic lava as an example, we are led to the probability that the bulk of water released in the eruption is associated with the ascending magma itself, in this particular case.*

Analogous experiments with granite show that, as the result of granite-water interactions, there is a parting of certain mineral fractions from the rock that are enriched with silica, alkalies, and alumina together with traces of magnesium and small amounts of calcium and iron.

Depending on temperature and pressure in the presence of water, the crystallizing fractions resemble the average type of granitic pegmatites with an excess of quartz, enriched with silica and alkalies, in reference to the original material (Table 7). These fractions of the pegmatitic type may contain more potassium than sodium or more sodium than potassium, depending on composition of the original granite.

Certain characteristics of water—the principal volatile substance—in reactions with the rock lead us to the supposition that there exists a single primary magma of a chemically basic character.

The foregoing experimental data show that the presence of water, in certain instances, leads to separations of solutions enriched by various groups of constituents of the original rock. The intensity and the orientation of these phenomena are determined chiefly by temperature, pressure, and time.

The experimental findings were determined in the presence of an excess of water, although this does not alter the fundamental course of the process; even when the content of water is lower the only difference is in the rate at which the rock-solution equilibria are to be attained.

Our experiments may serve to illustrate a type-composition of the gaseous-liquid fraction co-existent with the solidifying melt, in the terminal stage of the life of the magma, in a mobile equilibrium both with the solid mineral phase and (mainly) with the end-products of the liquid melt reflecting thereby the very essence of these terminal melts. Depending on the degree of the crystallization, chemical composition of this fraction of the melt must be subject to variations in time.

Consolidation of the melt into rock, in time, takes place at different rates, which depend on its geologic environment as a whole. Concurrently with this process, for every interval of the time, the following are characteristic: early minerals in the solid phase; a residual fraction of the magmatic solution in the liquid phase; a gaseous phase. As to the temperature—it should be lower than 1000°C for the vast bulk of the rocks, since experimental evidence on melting temperatures of rocks, in the presence of water, indicates that the temperatures in question are below the 1000° threshold.

If volatile constituents play a tremendous role in the redistribution of substance by thermal diffusion during the early magmatic stages, *their role is even more decisive during the crystallization stage of the process, which means, first of all, the role of water.* During this latter stage in the life of any type of a magmatic solution, when a certain fraction of its solid phase comes into being, as the result of cooling, and the residual solution acquires a greater mobility, because of its enrichment with water, the water functions not only as an aid to the differentiation, but also as one of the principal regulators of this later process.

Table 7

Constituent	Biotite-Hornblende Granite, Kavak-Tau, Kirgiziya						Porphyry-like Biotite Granite, Tyrry-Auz, Caucasus		
	T = 400°C.; P = 800 atm.		T = 400°C.; P = 3500 atm.		T = 650°C.; P = 3000 atm.		T = 600°C.; P = 3000 atm.		Average chemical composition of pegmatite-schist granite*
	Original granite	Mineral fraction of condensate	Calculated composition	Mineral fraction of condensate	Calculated composition	Mineral fraction of condensate	Original granite	Mineral fraction of condensate	
SiO ₂	74.4	88.4	13 + 75.4	89.0	14 + 75.0	92.3	74.5	95.0	74.67
Al ₂ O ₃	13.3	4.7	10.0	2.5	6.0	5.9	14.2	3.4	14.22
Fe ₂ O ₃ + FeO	2.0	0.3	0.6	0.1	0.2	--	1.9	0.05	0.44
CaO	1.9	1.4	2.9	0.8	1.8	0.1	1.6	0.1	1.11
Na ₂ O	3.2	2.3	4.8	3.1	6.8	0.6	4.2	1.0	3.20
K ₂ O	5.2	2.9	6.3	4.5	10.2	1.1	3.6	0.5	6.36
Sum	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Note: The SiO₂ in the "Calculated Composition" columns is broken down into two parts: (a) the part which is referred to the pegmatite at 75% SiO₂; (b) the residue,

The progress of the differentiation is determined by its geologic environment which controls the entire process of consolidation of the magmatic material into rock, whether under conditions where the material is more or less confined or its confinement is disrupted occasionally or periodically. In the first case, cardinal importance is accorded by the thermal-diffusion phenomena conducive to a segregation of the mobile water-rich residue, whereas, in the second case, it is determined by a simple out-flow or a squeezing of the material into the tectonically weakened surrounding zones.

The general course of rock formation in the "mainline" series appears to be successive transformations of the primary magma, particularly when its crystallization is taking place in the presence of variations in the $H_2 - Fe - H_2O$ system.

In the light of the foregoing considerations, we are led to a conclusion that the preponderance of ultrabasic varieties of rock in the intrusive series may be most easily explained by the natural process of their formation with an active participation of water in the crystallization of the primary magma, when a most energetic redistribution of the liquid melt is taking place amidst the already crystallized refractory combinations of minerals. This redistribution is accompanied by a withdrawal of the mobile water, together with the acid melts, and by a measure of enrichment of the ultrabasic residue by hydrogen; it is in this residue that the iron is accumulated. Ultrabasic rocks are remnants of the original primary basic magma which was reworked by volatile substances during crystallization in different structural horizons, depending on geologic environments.

The appreciable role of water in the formation of igneous rocks may be further sustained, to a degree, by the specific variations in the O^{18} isotopic ratios. The recent data by A. P. Vinogradov, E. I. Gerasimova, and M. S. Chupakhin [6] confirmed the existence of the progressively increasing scattering of this isotopic ratio, from the abyssal ultrabasic rocks toward the acidic formations, and demonstrated the scattering of the ratio in the systematically chosen test materials (see 8).

The fact of the regularly oriented dispersion of the O^{18}/O^{16} isotopic ratio serves to indicate the orientation of the natural process itself which is conducive to the formation of the chief representative igneous series, and which is accompanied by isotopic exchanges of oxygen, with water functioning as the main carrier of oxygen.

The findings of S. R. Silverman [7]

are important, in this connection, as they serve to define the range of the O^{18} fluctuations both in basic and acidic rocks. Silverman points out that this range is very narrow in the basic rocks, whereas in the acid series there is a great deal of scattering of the ratio; in his opinion,

Table 8

Rocks	Average O^{18}/O^{16} ratio
Dunites	490.0 ± 0.1
Basalts	489.5
Granites	488.7

there are the corresponding differences in the rock-forming environments of the basic and the acid series. Moreover, all such conditions are most likely to be dependent significantly on the participation of oxygen itself (as water) in the formation of igneous rocks as a whole. There is a lot more oxygen taking part in the development of the acid differentiates of igneous rocks than in the development of basic rocks. This difference is reflected in the course of the isotopic exchanges. Consequently, there are certain indirect indications of the importance of water in the formation of igneous rocks also in the data reported in the present article.

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DETERMINATION OF AGE OF SOME MICAS BY
THE RUBIDIUM-STRONTIUM METHOD

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Abstract

Nine new age values for micas obtained by the rubidium-strontium method are given; the method of isotopic dilution is used for the determination of rubidium and strontium. The method of chemical treatment of the micas is described. It has been shown that between the data of the rubidium-strontium and the potassium-argon method of age determination a better agreement is obtained if the β -decay of Rb^{87} the decay constant equal to $1.39 \times 10^{-11} \text{ year}^{-1}$ and for K-capture of K^{40} the value of $5.5 \times 10^{-10} \text{ year}^{-1}$ are used. In two cases a divergence between the data of the potassium-argon and the rubidium-strontium method for age determination was observed which is obviously due to the recrystallization of micas.

As we know, the beta-decay of rubidium, discovered by Thomson in 1928, leads to the formation of a stable isotope of strontium which accumulates, in time, in rubidium-bearing minerals. Hemmendinger [1], Smythe [1], Hahn, Strassman and Wollig [2], and Mattauch [3] showed that the active rubidium isotope has the mass of 87 and that it yields Sr^{87} on its decay. Yu. M. Tolmachev and A. N. Filippov [4] in 1954 made the first attempt in the USSR to determine strontium in the rubidium-bearing amazonites.

V. M. Goldschmidt, in 1937 [5], suggested the suitability of radioactive rubidium for determining the geologic age of minerals. Minerals suited for determination of their age by this method should be high in rubidium but low in non-radiogenic strontium. According to Goldschmidt [6], such rubidium-strontium ratios are to be found in potassium minerals belonging to the late crystallization stage of pegmatites in which K ($1.33 \text{ \AA}$) is replaced by Rb ($1.49 \text{ \AA}$). There is very little radiogenic strontium in such minerals because its bulk is accumulated in minerals formed in the earlier stage of the crystallization. The enrichment of rubidium attains its peak in lepidolites, where it may be as high as several per cent. These minerals, as a rule, contain practically no non-radiogenic strontium, which makes them especially valuable in determinations of age.

According to Ahrens [7, 8], not only lepidolites but also some other minerals are suited for age determinations by the strontium method: microcline, pollucite, phlogopite, muscovite, rhodochrosite, and cesium

beryl. Ahrens points out that biotite too may be employed, as it contains generally 0.1 to 0.2% rubidium. Such amounts of rubidium are found in biotite from ordinary pegmatitic veins. As to biotites from pegmatitic-lithium complexes—their rubidium content is appreciably higher and may be up to nearly 2%, according to Stevens and Schaller.

The mass-spectrographic isotopic analysis of strontium isolated by Strassman and Wollig [14] was performed by Mattauch. The result showed that practically all of this strontium is radiogenic. As a result of their findings, Hahn and Wollig [10] concluded that it is possible to make use of the radioactivity of rubidium in determining the age of ancient geologic formations.

Later on, several investigators employed this method in their determinations of the age of individual minerals [11]. Ahrens [12] especially had made a large number of determinations by spectrographic analysis for Rb and Sr. This analysis, however, is suited for the purpose only in cases in which 90% Sr in the mineral is of radiogenic origin.

The rubidium-strontium method remained inadequately developed a long time because of certain analytical difficulties in the exact determinations of small quantities of both rubidium and strontium. These difficulties were overcome successfully by the introduction of the isotope-dilution procedure. This procedure was applied for the first time in 1952 by Aldrich [13].

It was shown by Aldrich that 0.01% rubidium and 0.0001% strontium in 0.1 g. of the test material, may be determined reliably in a mass-spectrometer of ordinary sensitivity by the means of the isotope-dilution procedure. He used Sr^{84} -enriched strontium and 70% Rb^{87} rubidium.

Table 1

Source of Pegmatite	Mineral	Age, 10^6 years	
		$\text{Pb}^{208}/\text{U}^{238}$	$\text{Pb}^{207}/\text{U}^{235}$
Bikita Quarry, S. Rhodesia, S. Africa	monazite	2640 ± 100	2680 ± 10
Lake Viking, Saskatchewan, Canada	uraninite	1790 ± 50	1830 ± 50
Bob Ingersoll Mine, Keystone, S. Dakota	uraninite	1580 ± 30	1600 ± 30
Cardiff Uranium Mine, Ontario, Canada	uraninite	1020 ± 20	1020 ± 20
Fission Mine, Wilberforce, Ontario, Canada	uraninite	1040 ± 20	1050 ± 20
Chestnut Mine, Spruce Pine, S. Carolina	uraninite	375 ± 10	380 ± 10

ing more sensitive mass-spectrometers, it is possible to reduce the quantity of the element by several orders of magnitude without impairing the reliability of the determination.

A large number of the age data obtained by the rubidium-strontium method has become available in the USA in recent years. Initially the calculations were with the aid of the Rb^{87} decay constant taken as $1.1 \times 10^{-11} \text{ year}^{-1}$ derived geochemically by Strassman and Walling [14] and believed to be the most reliable one until now. The age results obtained were found to be 25 to 30% higher, in all instances, than the earlier results obtained by the lead and by the argon methods. In order to ascertain the cause of such discrepancies, the American investigators decided to re-determine the constant of rubidium decay. As we know, a direct determination of this constant for Rb^{87} , by the counting methods, is extremely difficult, because of the low energy of the β -particles emanating from Rb^{87} . This difficulty is responsible for the variations in the constants determined by different investigators [15].

Having taken all of this into account, Wetherill, Tilton, and Davis [16] decided to redetermine the constant of the β -decay of Rb^{87} by means of chemical methods. They determined the content of Sr^{87} and Rb^{87} of various minerals whose age was established reliably by the lead method and calculated the decay constant for Rb^{87} from their findings. Their findings and the results for the decay constants of Rb^{87} are presented in Table 1. The average value of the constant $1.39 \times 10^{-11} \text{ year}^{-1}$ may be adopted as the most reliable one.

In the same year, Fritze and Strassman [17] also undertook to determine the decay constant for Rb^{87} geochemically, on the basis of the

Table 1 (Continued)

Name of Pegmatite	Mineral	$\text{Sr}^{87}/\text{Rb}^{87}$	$T_{1/2} \text{Rb}^{87}$ $\times 10^{10} \text{ yrs.}$	$\lambda \times 10^{11} \text{ yrs.}$
Quarry, Rhodesia, S. Africa	lepidolite	0.0380 ± 0.0010	5.0	1.39
Viking, Athabasca, Canada	biotite	0.0270 ± 0.0010	4.8	1.44
Ingersoll Mine, Blackstone, S. Dakota	lepidolite muscovite microcline	0.0239 ± 0.001 0.0244 ± 0.001 0.0140 ± 0.0007	4.8	1.44
Buff Uranium Mine, Theriot, Canada	biotite	0.0140 ± 0.0007	5.1	1.36
Wanapiteon Mine, Wilberforce, Ontario, Canada	muscovite	0.00515 ± 0.0002	5.2	1.33
Wanapiteon Mine, Spruce Pine, S. Carolina	microcline	0.00535 ± 0.0002	5.0	1.39

age constants obtained by the argon method. This determination of the decay constant is not very reliable, because it is based also on the ratio which is too low: $\lambda_e K^{40} / \lambda_\beta K^{40} = 0.087$.

Having obtained the new value for the Rb^{87} decay constant, American investigators began to apply the rubidium-strontium method to minerals within the age limits from tens of millions to 2.5×10^9 years, and higher. At the same time, there were studies in comparisons between the ages of data obtained by the rubidium-strontium and by potassium-argon as well as by the lead methods. We may refer, in this connection, to the report by Hurley, Fairbairn, and Cormier [18], who made a comparison between the potassium-argon and the rubidium-strontium methods. Their results are presented in Table 2, indicating a good agreement between the two methods. Tilton, Davis, Wetherill, and Aldrich [19] report the age of minerals as determined by the lead, the strontium, and the argon methods. Their results are cited in Table 3. The table illustrates the

Table 2

Source of Granite	Age by Ar/K 10^6 years	Age by Sr/Rb 10^6 years	Ratio
Conway, New Hampshire	175	170	1.04
Larris River, Nova Scotia	320	330	0.97
Albany Cross, Nova Scotia	385	365	1.05
Lake Guernero (?), Nova Scotia	390	370	1.05
Beer River, Nova Scotia	390	370	1.05
Ship Harbor, Nova Scotia	390	400	0.98
Grayton, Sudbury, Ontario	1360	1245	1.09
Rockwill, Minnesota	1690	1620	1.04
St. Cloud, Minnesota	1860	1775	1.05
Sacred Hat (?), Minnesota	2530	2330	1.08
Average	--	--	1.04

good agreement between the argon and strontium methods. The age data for zircons obtained from the ratio Pb^{207}/Pb^{206} are also in agreement with the foregoing results. Discrepancies between the age, as calculated from the ratios: Pb^{206}/U^{238} , Pb^{207}/U^{235} , Pb^{207}/Pb^{206} , and Pb^{208}/Pb^{232} , for certain minerals, is ascribed by the authors to the metamorphism of the test specimens. The micas, however, were not subject to the metamorphism.

A paper was published in 1957 calling attention to two examples of discrepancies between the potassium-argon and the rubidium-strontium methods [20]. The especially interesting case is the one where the age calculated from the Ar/K ratio exceeds the age obtained by the rubidium-strontium method. This case makes it difficult to interpret the results obtained. The reasons for the discrepancy remain obscure; their explanation requires additional radiometric as well as geologic studies.

Table 3

Sample	Age of Zircon, Million Years				Age of Micas, Million Years	
	U ²³⁸ /Pb ²⁰⁶	U ²³⁵ /Pb ²⁰⁷	Pb ²⁰⁷ /Pb ²⁰⁶	Th ²³² /Pb ²⁰⁸	Rb ⁸⁷ /Sr ⁸⁷	K ⁴⁰ /Ar ⁴⁰
Redstone, New Shire	187 ± 5	184 ± 5	140 ± 60	190 ± 5	185	182
egmatite, Wichita, oma	520 ± 12	527 ± 10	550 ± 30	506 ± 12	500	480
egmatite, Wichita, oma	514 ± 12	522 ± 10	550 ± 20	493 ± 12	-	-
r, Tory Hill, Ontario	1030 ± 25	1050 ± 15	1080 ± 25	390 ± 15	-	-
r, Capetown, ica	330 ± 10	356 ± 15	530 ± 50	238 ± 20	600	530
r, Tory Hill, Ontario	940 ± 25	960 ± 15	1015 ± 25	-	-	-
ite, Uranium Mine, ff, Ontario	900 ± 25	930 ± 15	1000 ± 25	990 ± 25	1030	1010
Bridge, Contact	1025 ± 25	1065 ± 20	1140 ± 50	-	-	-
r, Pike's Peak, Colo.	625 ± 25	707 ± 20	980 ± 40	313 ± 12	1020	1030
r, Llano, Texas	950 ± 25	990 ± 15	1070 ± 25	890 ± 40	1100	1090
r, Bagdad, Arizona	630 ± 20	770 ± 30	1210 ± 80	271 ± 16	1390	1410
r, "A", Quartz Creek, ado	925 ± 25	1130 ± 35	1540 ± 140	530 ± 110	-	-
r, "B", Quartz Creek, ado	-	-	1700 ± 60	-	1310	1325

one may see from this brief review that the rubidium-strontium method is now used fairly extensively abroad in determinations of the ages of minerals.

According to some scientists this is the very method that offers the maximum of reliability for dating of ancient rocks. Inasmuch as the Laboratory of Precambrian Geology, Academy of Sciences of the USSR, has an interest in the geology of the Proterozoic and the Archean ancient formations, it appeared reasonable to us to make use of the strontium-rubidium method in determining the ages of such ancient formations.

PROCEDURE

The aim of our study was to obtain new data on the age of certain rocks by the rubidium-strontium method and to compare them with the data obtained by the potassium-argon method.

We made use of the isotopic-dilution procedure in determining Rb⁸⁷. Analytically, the most reliable procedure, in our opinion, which was complemented on occasions by parallel gravimetric determinations, by the Vells-Stevens method, as refined by us, involving the use of a radioactive indicator [21].

The isotopic dilution procedure is based on the addition, to the test material, of an exact quantity of the element of isotopic composition which differs from its isotopic composition in the earth's crust. Knowing the amount of the stable isotope added to the sample as an indicator,

it becomes possible to calculate the amount of the given element in the test material from the change in the isotopic composition of the mixture. The advantage of the isotope-dilution method is that it does not require a complete purification of the element which is being determined. Rb^{87} -enriched rubidium and Sr^{84} -enriched strontium were used by us as the indicators.

The concentration of these solutions was determined both gravimetrically and by the MS-2M mass-spectrometer, by reference to standard solution of ordinary rubidium and strontium salts. One such determination, for example, is reported in Table 4. The average of several determinations was taken as the standard.

Table 4

$\text{Rb}^{85}/\text{Rb}^{87}$ Ratio		
K_1 , in common Rb	K_2 , in Rb indicator	K_3 , in the mixture of 2.02×10^{-5} grams of common Rb^{87} and 0.9903 grams of the indicator solution
2.588	0.130	0.850

$\text{Sr}^{84}/\text{Sr}^{88}$ Ratio		
K_1 , in common Sr	K_2 , in Sr indicator	K_3 , in the mixture of 7.17×10^{-5} grams of common Sr^{88} and 1.9924 grams of the indicator solution
0.00678	1.93	0.238

From the equations:

$$\text{Rb}^{87}_{\text{mix.}} = \text{Rb}^{87}_{\text{com.}} \frac{K_3 - K_2}{K_1 - K_3} \quad \text{and} \quad \text{Sr}^{84}_{\text{mix.}} = \text{Sr}^{88}_{\text{com.}} \frac{(K_3 - K_1) K_2}{K_2 - K_3} \times \frac{84}{88}$$

The concentrations of the solutions are calculated as:

$$\text{Sr}^{84} = 9.03 \times 10^{-6} \text{ g. per 1 g. of the solution}$$

$$\text{and } \text{Rb}^{87} = 4.92 \times 10^{-5} \text{ g. per 1 g. of the solution.}$$

We made no use of the commonly used procedure of decomposing the mineral with a mixture of H_2F_2 and HClO_4 , with the subsequent isolation of the perchlorates by adsorption on a cationite, in our determinations of rubidium and strontium, for the following reasons. It is known from the literature that double fluorides of potassium or rubidium are very stable, sparingly soluble compounds that cannot be decomposed completely even by boiling with HClO_4 [22]. The presence of fluoride sediments in the test solution may interfere with the complete inter-mixing of the added rubidium and strontium indicators with the isotopes of

se elements we are trying to determine. This is especially important in the analysis of large aliquots. With these considerations in mind, we made use of the following procedure in the treatment of our minerals:

In the determination of rubidium, an aliquot of mica (0.02 to 0.50 g.) is decomposed either by sintering, as in the ordinary Smith procedure, or by acids ($\text{H}_2\text{F}_2 + \text{H}_2\text{SO}_4$), by the procedure of Berzelius. The latter method is preferable, because the tagged isotope, Rb^{87} , is added to the test material at the very start.

Samples decomposed by the Smith method were reduced to a mixture of the alkali metals, as usual were mixed with the indicator solution of Rb^{87} , and, after their conversion to sulfates, were used for the isotopic investigation. Samples decomposed by acids received their indicator from the start. After the removal of silica, it was enough merely to ignite them, to filter off the water-insoluble residue, and to determine rubidium in the filtrate.

The filament of the ion-source, carefully washed, was burned in *vacuo* and was tested for the absence of rubidium in a mass-spectrometer prior to the placement of the test material on the filament. The measurements were made with the ordinary single-filament source making use of the surficial ionization. Dimensions of the tungsten filament were 0.030 x 0.8 x 12 mm.

In the determination of strontium, an aliquot of mica (generally 0.000 to 1.000 g.) was decomposed by a mixture of hydrofluoric and perchloric acids. A measured quantity of the indicator solution of Sr^{87} was added at the same time the solution with the sediment was evaporated. The treatment was repeated several times.

The evaporation was down to the moist-salt stage. The residue in the dish was treated with hydrofluoric acid (1:2 or 1:3). The fluoride residue was centrifuged and washed with water with some H_2F_2 . As a result of repeated verifications by the means of the added indicator Sr^{87} , we became convinced that SrF_2 is to be found in the fluoride residue, in this stage of the procedure, as it becomes separated from the oxides of aluminum and iron (some aluminum and some iron stay in the residue, as double fluorides of K and Rb).

The isolated fluorides were decomposed by 5% aqueous NaOH, in the presence of Na_2CO_3 , whereupon aluminum passes into the solution. The precipitant is washed with water and is dissolved in HCl.* The solution is evaporated to dryness and the residue is dissolved in 0.4N HCl; the solution is passed through a column of the KU-2 cationite, in its H form, under conditions of the procedure developed by E. K. Gerling and Yu. A. Polyukov [23] for the isolation of strontium by means of the CDV-3 cationite.

The sediment is bulky, as may be the case where large aliquots of test materials are used (up to 10 g.), we used an additional step in the concentration of the precipitation of sulfates.

The elution was done by 2.5N HCl. Fractions of the extract containing strontium were combined (Sr^{89} was used as the control), evaporated, and, following ignition, the evaporated residue was converted into nitrate. Strontium nitrate was transferred onto the filament of the ionization source. A two-filament source was employed in the isotope analysis [24, 25]. One of the filaments functioned as the volatilizer; the other one as the ionizer. The volatilizer was placed 1.5 to 2 mm from the ionizer, at 45° angle to the ionizer. Dimensions of the filaments were as follows: Volatilizer: $0.030 \times 0.5 \times 11$ mm; ionizer: $0.030 \times 0.7 \times 11$ mm. From the source of such design, strontium escapes in the form of single-charge ions.

The amounts of Rb^{87} and Sr^{87} in minerals were calculated by us from the experimental data, with the use of the following equations:

$$\text{For strontium, } \text{Sr}^{87}_{\text{rad.}} = \text{Sr}^{84}_{\text{ind.}} (1/K_1 K_2 - 1/K_5 - 1/K_2 K_3 - 1/K_3 K_4) 87/84, \text{ where}$$

$$K_1 = \text{Sr}^{88}_{\text{mix.}}/\text{Sr}^{87}_{\text{mix.}}; K_2 = \text{Sr}^{84}_{\text{mix.}}/\text{Sr}^{88}_{\text{mix.}}; K_3 = \text{Sr}^{88}_{\text{com.}}/\text{Sr}^{87}_{\text{com.}} = 11.76$$

the ratios sought for the test material

$$K_4 = \text{Sr}^{84}_{\text{ind.}}/\text{Sr}^{88}_{\text{ind.}} = 0.93; K_5 = \text{Sr}^{84}_{\text{ind.}}/\text{Sr}^{87}_{\text{ind.}} = 14.65.$$

for the given indicator.

Hence:

$$\text{Sr}^{87}_{\text{rad.}} = \text{Sr}^{84}_{\text{ind.}} (1/K_1 K_2 - 0.0850/K_2 - 0.0242) 87/84.$$

$$\text{For rubidium } \text{Rb}^{87} = \text{Rb}^{87}_{\text{ind.}} (K_3 - K_1/K_2 - K_3),$$

$$\text{where } K_1 = \text{Rb}^{85}_{\text{ind.}}/\text{Rb}^{87}_{\text{ind.}} = 0.130; K_2 = \text{Rb}^{85}_{\text{com.}}/\text{Rb}^{87}_{\text{com.}} = 2.588$$

for the given indicator

for the common rubidium

$$K_3 = \text{Rb}^{85}_{\text{mix.}}/\text{Rb}^{87}_{\text{mix.}}$$

the ratio sought for the test mixture.

$$\text{Hence: } \text{Rb}^{87} = \text{Rb}^{87}_{\text{ind.}} (K_3 - 1.130/2.588 - K_3).$$

The results obtained by us for several specimens of micas are reported in Table 5. The maximum error of the determination, including the error of determination of the indicator's concentration, is $\pm 6\%$ for Sr^{87} .

With the exception of two specimens, Nos. 265 and 614, the content of radiogenic strontium in the micas was 90 to 99% as of the total strontium in the mineral. We must consider here, however, that a certain quantity of common strontium was introduced into the test materials together with the reagents and with the radioactive indicator.

Table 5

Sample No.	Description and source	Determination of Sr^{87}				Determination of Rb^{87}					Remarks
		Aliquot, g.	Tagged Sr^{84} added 10^{-5} g.	Ratio Obtained $88/87$	Ratio Obtained $87/88$	Radiogenic Sr^{87} , 10^{-2} %	Aliquot, g.	Tagged Rb^{87} added, 10^{-5} g.	Ratio Obtained $85/87$	% Rb^{87}	
359	Muscovite; Trench No. 1701, Mt. Polmas, Kola Peninsula	0.5000 0.5000	4.498 4.511	0.338 0.367	1.74 1.68	1.52 1.45 Av. 1.49	0.0500 0.5000	48.4 -	0.897 -	0.437 0.456 Av. 0.447	Gravimetric
356	Muscovite; Vein No. 2, Trench No. 10, Kolnozersk Deposit, Kola Peninsula	0.5000 0.5000	3.623 3.610	0.520 0.502	1.66 1.71	0.812 0.815 Av. 0.813	0.0500 0.5000	38.5 38.5	0.730 0.721	0.244 0.248 Av. 0.246	-
360	Muscovite; Vein No. 18, Trench No. 313, Vasin-Myk, Voronya Tundra, Kola Peninsula	0.2500 0.2500	6.340 6.270	0.369 0.386	1.87 1.73	3.68 3.69 Av. 3.69	0.0500 0.0200	72.2 48.6	1.126 0.865	0.99 1.04 Av. 1.02	-
357	Lepidolite; the Vasin-Myk Vein, Kola Peninsula	0.2500 0.2500	9.023 9.037	0.420 0.385	1.76 1.82	4.78 5.07 Av. 4.92	0.5000 0.5000	35.0 -	0.649 -	1.91 1.85 Av. 1.88	Gravimetric
265	Mica from beryl-pegmatite; Bolshoy Lapot Lake, Kola Peninsula	0.5000 0.5000	3.607 2.825	1.59 2.92	1.60 0.84	0.236 0.227 Av. 0.232	0.0500 0.0500	19.2 19.2	0.506 0.495	0.0695 0.0668 Av. 0.0681	
268	Mica from pollucite pegmatite, Vasin-Myk Vein, Kola Peninsula	0.5000	8.976	0.320	1.78	3.13	0.5000 0.5000	11.7 11.6	0.861 0.874	1.01 1.04 Av. 1.03	
289	Muscovite from pegmatitic veins; Mt. Bezymyannaya, Kolmogorsk Deposit, Kola Peninsula	0.5000	1.798	0.390	1.54	0.590	0.5000	5.75	0.722	0.187	
13. 6	Muscovite; Mama District, Siberia	10.000	3.628	5.30	0.29	0.0125	0.5000	48.4	0.574	0.0214	
614	Specimen 1984/1090; mica-garnet schist; vicinity of Polyarnyi City, Belokamennaya	3.0000 3.0000	3.748 1.864	6.20 4.70	0.31 0.28	0.0286 0.0277 Av. 0.0282	1.0000 0.5000	48.3 23.8	0.529 0.544	0.00940 0.00962 Av. 0.00951	

Table 6

Sample No.	Description and Source	Determined Age (10^6 years)		
		By $\text{Sr}^{87}/\text{Rb}^{87}$	By $\text{Ar}^{40}/\text{K}^{40}$	
		$\lambda = 1.39 \times 10^{-11}$	$\lambda_e = 5.49 \times 10^{-11}$ $\lambda_\beta = 4.72 \times 10^{-10}$	$\lambda_e = 6.02 \times 10^{-11}$ $\lambda_\beta = 4.90 \times 10^{-10}$
359	Muscovite; Trench No. 1701; Mt. Polmas, Kola Peninsula	2400 ± 190	2000 ± 50	1880 ± 50
356	Muscovite; Vein No. 2, Trench No. 10, Kolmozersk Deposit, Kola Peninsula	2380 ± 190	1740 ± 50	1630 ± 50
360	Muscovite; Vein No. 18, Trench No. 313, Vasin-Mylk, Voronya Tundra, Kola Peninsula	2600 ± 200	2350 ± 50	2200 ± 50
357	Lepidolite; the Vasin-Mylk Vein, Kola Peninsula	1880 ± 150	2110 ± 50	1980 ± 50
265	Mica from beryl pegmatite; Bolshoi Lapot Lake, Kola Peninsula	2450 ± 190	1830 ± 50	1710 ± 50
268	Mica from pollucite pegmatite; the Vasin-Mylk Vein, Kola Peninsula	2190 ± 180	2100 ± 50	1970 ± 50
289	Muscovite from pegmatitic veins; Mt. Bezmyannaya, Kolmogorsk Deposit, Kola Peninsula	2270 ± 180	2350 ± 50	2200 ± 50
13/6	Muscovite; Mama District, Siberia	420 ± 55	367 ± 20 364 ± 20	336 ± 20 333 ± 20
614	Specimen 1984/1090; mica-garnet schist; vicinity of Polyarnyi City, Belokamennay Guba, Murmansk District	2130 ± 170	1810 ± 50	1700 ± 50

There was only 8% radiogenic strontium in mica specimen No. 614. This specimen from a schist was very high in calcium.

The age was calculated from the following equation:

$$t = (\% \text{Sr}^{87} / \% \text{Rb}^{87} \text{ rad.}) \times (1/\lambda),$$

where λ was taken as $1.39 \times 10^{-11} \text{ year}^{-1}$.

The calculated age data are summarized in Table 6, which includes also the results obtained by the potassium-argon method for the sake of comparisons, by using two different constants.

The table shows that the age data obtained by the potassium-argon method, using the constant of $5.5 \times 10^{-11} \text{ year}^{-1}$, are in better agreement with the data obtained by the strontium method than when the $6.0 \times 10^{-11} \text{ year}^{-1}$ constant is used.

In two instances, specimens Nos. 356 and 265, the argon method yielded results that were too low. This lowering may be related to some effects of a later magmatism upon the micas by which they may have been subjected to a recrystallization and the consequent loss of argon they had accumulated in the past. According to M. M. Ermolov, a recrystallization of micas may have taken place in the Kolmozersk district, where we have evidence of a later magmatic activity associated

the epoch of the Karelian diastrophism. In this District the age results obtained by the argon method are significantly too low. Most of our age data, both by the rubidium-strontium and the potassium-argon methods, are within the range of 2000×10^6 to 2400×10^6 years, which indicates an exceptionally great age of the pegmatitic micas. The veins in question are much older than the Karelian formations (1800×10^6 years).

Specimen No. 13/6 was taken from a mica pegmatite, Mama District, Kola Peninsula. This mica, geologically, is either Upper Archean or Lower Proterozoic. This thesis is not sustained, it appears, by the age results as given by the potassium-argon or the rubidium-strontium methods. The age of specimen No. 614, a mica from a schist, Kola Peninsula, as given by the rubidium-strontium method, merits special attention. It exceeds the age given by the argon method, possibly for the following reasons.

We know that the formation of micas in schists derived from gneisses involved a metamorphism of clayey sediments included in the general structure of the rock. During the metamorphism, these sediments lose practically all of their accumulated argon to the gaseous phase. Radiogenic strontium, on the other hand, accumulated by the same sediments, one would think, in its entirety becomes a constituent of the micas that are produced in the metamorphism. If so, it should be possible to calculate the time elapsed since the formation of the clayey sediments from the Rb^{87} ratio in the micas and to calculate the age of the metamorphism of the sediments from the Ar^{40}/K^{40} ratio. This suggestion needs to be tested, however, against a large body of geologic materials, as we have to do in 1958-59.

Summarizing the foregoing, in brief, we may draw the following conclusions:

The age of the pegmatitic veins in the Kola Peninsula is within the range of 2×10^9 to 2.40×10^9 years, by the rubidium-strontium method.

The rubidium-strontium and the potassium-argon methods agree if the β -decay constant for Rb^{87} is taken as $1.39 \times 10^{-11} \text{ year}^{-1}$ and the electron-capture constant for K^{40} as $5.5 \times 10^{-10} \text{ year}^{-1}$.

Micas from pegmatitic veins of the Mama District are shown to be younger, both by the rubidium-strontium and by the potassium-argon methods, than they were believed to be by geologic evidence.

A discrepancy between the rubidium-strontium and the potassium-argon methods, as to the age of micas, in two instances, may be due to recrystallization of the micas.

In conclusion, it is our pleasant duty to express our gratitude to M. M. Zaslavskiy for his aid in the discussion of our results and for the specimens of rubidium-rich micas he has kindly placed at our disposal.

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ON DETERMINATIONS OF THE ABSOLUTE AGE OF THE ORE DEPOSITS OF THE URALS

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Abstract

Determinations are given of the absolute geological age of micas and feldspar from metasomatic rocks accompanying contact-metasomatic Cu and Fe, and other deposits of the Urals, carried out by the potassium-argon method. Genetic relations of the individual deposits to intrusive massifs have been outlined, and Metallogenetic stages of ore deposit formation in the Palaeozoic have been established. These stages reflect the corresponding stages of magmatic activity and definite phases of orogenesis. The metallogenetic stage (420-460 million years) corresponds to the Salair phases, the middle-Palaeozoic stage (320-360 million years) to the Taconian phases, the upper-Palaeozoic stage to the Hercynian phase (248-270 million years).

The radioactive procedures for determining the absolute age of ore deposits continue to penetrate still deeper into different fields of geology. It is difficult to overestimate their value in geochronology, stratigraphy, tectonism, and metamorphism. Their importance in studies of mineral deposits is just as great. Together with direct determinations of the time at which the given deposit was formed, absolute age methods can be employed as major aids in studies of the origins of ores as well as in the exploration for them.

Ore-forming environments and distribution-abundance relationships of magmatic deposits of iron, copper, titanium, vanadium, chromium, cobalt, platinum, and of certain rare elements are especially important in the Urals, to understand. Deposits of these metals are represented here by several most important genetic types and belong, by the accepted classification, to the magmatic (in the strict sense) and, finally, to the contact-metasomatic, the hydrothermal, and the pegmatitic categories.

The argon method is particularly well suited for determination of the time at which post-magmatic deposits were formed, on the absolute geological scale, because potassium is one of the principal constituents of magmatic ore-forming solutions and because potassium metasomatism is a common alteration process in rocks close to ores, in host rocks containing contact-metasomatic iron ores and copper ores, pyrites and vein ores of copper, gold, tungsten, and others. In the case of rare-metal pegmatites, the lead method is just as valuable as

the argon method, because of the accumulation of uranium and thorium in pegmatites. The strontium method is also applicable to pegmatites.

Applications of the argon method and of the other methods here enumerated are not as satisfactory in the case of the very large group of magmatic deposits within basic and ultrabasic rocks where potassium minerals are scarce and where uranium, thorium, and rubidium are at their lowest levels. The possibility of applying the helium method has to be considered in problems of this sort. Because of its low ultra- and micro-porosity and because of its relatively high density [6], high temperature magnetite in magmatic deposits may assure satisfactory conservation of helium.

Some of the data at our disposal allow us here to cite concrete examples of the application of the absolute age measurements to various problems involved in the studies of the ore deposits of the Urals. Without any reservations, all our discussions and conclusions, based on a small number of the first significant figures, are tentative and must be regarded only as a means of posing the problems. For the sake of convenience, all of our comparisons of age data for various deposits of the Urals are summarized in one table. The data on the iron ores of Mt. Vysokaya, Mt. Blagodat, and Mt. Magnitnaya are taken from the report by Hurley and Goodman [14] who had already determined the age of their magnetites by the helium method in 1943. All of the rest of the data were obtained by the argon method in our laboratory [7, 8]. The samples examined were from our collection as well as those of V. A. Prokin, G. S. Ilyasov, G. F. Chervyakov, A. V. Gorokh, S. N. Ivanov, N. D. Rakcheev, and V. P. Loginov.

Endogenic deposits of the Urals are associated with Paleozoic metamorphism. We know very little about Precambrian volcanism in the Urals and nothing whatsoever about Precambrian metallogeny. Absolute age methods should be very useful to us in our studies of the Uralian Precambrian and of its possible metallogeny. It is probable, for example, that the small bodies of so-called ferruginous quartzites, so abundant in the metamorphic rocks of the Ufa Amphitheatre, are indeed very ancient. As indicated by the fairly convincing data assembled by G. V. Vertushkin, such accumulations of quartz-magnetite rock in the Mavrovo District were subjected to a severe granitization, including a complete replacement to granite gneiss, analogous to the rocks somewhat farther south, whose age was determined as Lower Proterozoic, about 1100-1150 million years [7]. Thus the iron ore deposits in question were formed either before or at the very beginning of the Proterozoic Age.

The numerous Paleozoic ore deposits are clearly divisible into three metallogenic stages, separated from one another by considerable time intervals. These metallogenic stages reflect corresponding stages of magmatic activity which are related, in turn, to certain definite phases of orogeny. The Lower Paleozoic stage corresponds to the Salair orogeny, the Middle Paleozoic stage to the subsequent phases of the Caledonian orogeny, the Upper Paleozoic stage to manifestations of the Harz orogeny.

the most ancient ones, among the Paleozoic deposits, are of magmatic origin and are localized in intrusions of gabbro-peridotite. We have age data only for the well known Pervouralsk deposit of titaniferous magnetite situated inside a gigantic hornblendite "schlier", in the Revda Intrusion. The Revda Intrusion is an integral part of the West-Plutonic Complex, of the so-called platiniferous gabbro-peridotite intrusion, which extends east-west, in the form of a chain of large massifs, for many hundreds of kilometers, along the border between the Ural Anticlinorium and sediments of the Greenstone Synclinorium.

The time of the formation of the Pervouralsk deposit, as indicated by the analysis of two late metasomatic minerals, hornblende and zircon, is determined at 455 million years, corresponding to the Cambrian, which helps us with differentiation of the Lower Paleozoic metallogenic stage. Judging by the only available determination of the age of the Pervouralsk massifs themselves, based on an analysis of a biotite gabbro in the Tagil Massif a little to the north, which was found to be 440 million years old, the titaniferous magnetite bodies were formed at the same time with their host rocks, which are also their genuine parents. Also, such a great age is an indication that the magmatic deposits of titaniferous magnetites were formed at a much earlier time than the magnetitic contact-metasomatic deposits and are not as intimately related to them as was assumed recently by some investigators [13].

The Middle Paleozoic metallogenic stage corresponds to the various stages of the Caledonian orogeny, which succeeded the Salair orogeny, associated with a very intensive magmatism, and is most highly enriched with ores. This stage played a major part in the development of the iron and copper deposits. The vast majority of the chalcopyrite and malachite deposits of the Urals belong to this stage.

The contact-metasomatic deposits reveal certain definite relations in their areal distribution in the Urals, as well as an association with a certain definite type of granitoid intrusions in the contact zones and the typical hypabyssal massifs wherein they are localized. As shown in the table, the time of origin of these deposits corresponds exactly to the time of formation of the genetically and spatially associated intrusions. Both the deposits and the intrusives are Silurian. Characteristically, the time of the formation of the intrusives and of the accompanying deposits is very close also to the time of the deposition of the intermediate volcanic rocks of their roof, which is pierced by the intrusions and in which the skarn ore bodies are developed by replacement. This fact is even more strikingly conspicuous in the formation of chalcopyritic deposits and is indicative of the very short time interval sufficient for complete development of any given section of the crust. The appearance of the intrusions, with the subsequent formation of the ores, came in the wake of the volcanic effusions, without any time interval at all, directly after pyroclastic and ordinary sedimentation and crumpling of these sediments into folds.

Table 1. Determinations of the Absolute Age of Minerals and Rocks from Ore Deposits of the Urals

Sample No.	Source and material	Ar ⁴⁰ /K ⁴⁰	Age, million years	Age of host rocks and of parent intrusives
I. The Lower Paleozoic Metallogenic Stage				
<i>A. Magmatic Deposits</i>				
27	Pervouralsk titanian magnetites. Hornblende and chlorite-zoisite-sericite metasomatic rock	0.0313	455	440 million years, biotite gabbro, Tagil Massif
<i>B. Chalcopyrite Deposits</i>				
1. Central Ural				
64	Kaban V. Sericitized overburden ("blanket") porphyrite	0.0314	460	Host rocks of Middle Ludlow age [4]
68	Krasnogvardeiskoe. Diaspore-sericite rock	0.0297	435	Host rocks assumed to be of Ludlow age
2. Southern Ural				
69	Gai (Gaiskoe). Quartz-sericite schist	0.0290	430	The host rock is referred to the Baimak-Buribai Suite of the Silurian [11]
70	Uchalinskoe. Quartz-sericite rock	0.0285	420	The host rock is referred to the Polyakovskaya Suite [2]
II. The Middle Paleozoic Metallogenic Stage				
<i>A. Contact-Metasomatic Deposits</i>				
-	Gora Blagodat. Magnetite (helium method), according to Hurley and Goodman, 1943	-	365	Age of the Kushvinskii syenite massif: 345 to 360 million years. The rocks are believed to be of Ludlow age
22	Valuevskoe Iron Ore Deposit, biotitic metasomatic rock	0.0240	360	Age of the Kushvinskii syenite massif: 345 to 360 million years. The rocks are believed to be of Ludlow age
-	Gora Vysokaya. Magnetite (helium method), according to Hurley and Goodman, 1943	-	340	Age of the Tagil Massif: 345 to 355 million years
19	Techenskoe Iron Ore Deposit. Metasomatic potassium feldspar—an alteration of porphyrites near the ore	0.0217	330	Age of the Kaldinskii Graptolite massif: 340 million years
<i>B. Chalcopyrite Deposits</i>				
11	Severnoe. Sericite schist	0.0211	320	
41	Yasvinskoe. Sericite schist	0.0220	335	
75	Maukskoe. Biotite schists; amphibolites altered near the ore zone	0.0234	350	The host rock is classified as Silurian
73	Yuzhno-Kuznechikhinskoe. Quartz-sericite schist	0.0211	320	The host rocks are classified as Silurian [10]
54	Karabash. Sericite schist	0.0233	350	The host rocks are classified as Upper Ludlow [2]

Table 1 (Continued)

Sample	Source and material	Ar ⁴⁰ /K ⁴⁰	Age, million years	Age of host rocks and of parent intrusives
	Novo-Karabash Log. Muscovite from chlorite-muscovite rocks associated with pyritic mineralization of serpentinites	0.0201	305	Serpentinites pierce limestones of the Euffel Tier
	Levikha X. Quartz-sericite schist	0.0253	375	The host rocks are older than Middle Ludlow [2]
	Levikha X. Sericite from contact seritization of a post-ore diorite porphyrite dike	0.0224	340	
	Sultanovskoe. Sericite-quartz rock	0.0222	335	
	Sultanovskoe. Kersantite	0.0228	340	
	Zyuzelskoe. Sericite from fissures in massive ore	0.0217	325	
	Zyuzelskoe. Sericite schist	0.0214	325	
<i>C. Pegmatitic Deposits</i>				
	Gora Slyudyanaya. Muscovite from Vein No. 4	0.0226	340	
	Gora Slyudyanaya. Allanite-bearing pegmatite from Vein No. 4	0.0206	310	
	Gora Slyudyanaya. Biotite schist near vein	0.0213	320	

III. Upper Paleozoic Metallogenic Stage

A. Contact-Metasomatic Deposits

Gora Magnitnaya. Magnetite (helium method), according to Hurley and Goodman

240-245

Age of the Magnitogorsk granodiorite massif: 340 million years

B. Chalcopyrite and Similar Deposits

Alekseevskoe (Neivo-Rudyanskoe). Quartz-sericite schist

0.0155

240

Imeni XIX Partseзда. Quartz-sericite rock

0.0172

265

Formed on the rocks of the Givais Tier [9] and older

Pyshma. Biotite near ore

0.0159

250

C. Gold Deposits

Bogomolovskoe. Mica schist near ore

0.0177

270

D. Pegmatitic Deposits

The Ilmenogorsk Complex. Lepidomelane from miaskite pegmatites

0.0172

265

Later than Lower Carboniferous

The Ilmenogorsk Complex. Granite pegmatites

0.0179

275

Later than Lower Carboniferous

Comparisons of the times when the contact-metasomatic deposits were formed with the times of formation of the adjoining intrusive massifs and of the roof rocks, where the ore deposits are localized, are possible on the basis of the direct determinations of the absolute age of the potassium minerals syngenetic with each of these geologic formations. Such direct measurements of the absolute age, together with the assembly of indirect geologic and geochemical indications, confirm also the genetic relationship of the deposits to the intrusions. A characteristic example of this relationship is the determined age of the recently discovered Techenskoe iron ore deposit situated away from any direct contact with any intrusion in the poorly known Eastern Synclinal Zone of the Central Urals. The relation of this deposit to the somewhat distant Kaldinskoe granitoid massif and their common adherence to the Caledonian stage are very well established by absolute age measurements for a diorite, 340 million years old, as compared to the age of a metasomatic potassium feldspar from the characteristic K-feldspathic halo surrounding the ore deposits in the still more ancient basic effusives. This feldspar is naturally somewhat younger; its age is 330 million years. It corresponds to the age of the ore deposition.

The single Caledonian age of the productive hypabyssal granitoid massifs, in the sense of contact-metasomatic mineralization, makes it possible to utilize the age determinations as one of the criteria of the productivity of the Uralian granitoids and to distinguish the productive Caledonian granitoids from Harz granites which, although they are not accompanied by any contact-metasomatic mineralization, may be rich in pegmatitic fields in several districts. Thus the age may serve as a definite prospecting criterion.

There is a certain vagueness about the status of the Mt. Magnitnaya deposit whose age was determined at 240 to 245 million years by Hurler and Goodman [14] using the helium method for the magnetite. This figure requires verification. Although we classified the Mt. Magnitnaya deposit as belonging to the Upper Paleozoic stage, in the table, its true age is Caledonian, in all probability, i.e., the same as the age of the Magnitogorsk intrusive body (with which the deposit is associated), of the metamorphic quartz-sericite rocks (the products of interaction of the intrusive body and the volcanic materials of the roof) and, finally, of the volcanic materials themselves.

The largest number of our determinations of the absolute age refer to the metamorphic formations accompanying the chalcopyritic deposits in the Central and Southern Urals. Large as it is, this number is still far from adequate for any serious conclusions, inasmuch as, so far, the origin of the pyritic deposits and their relation to the various igneous rocks is still among the most highly involved problems in the geology of the Urals. Nevertheless, it is possible to reach certain tentative conclusions. On one hand, our results confirm the generally accepted view regarding the ancient (Pre-Harz) age of these pyritic deposits, whereas, on the other hand, they indicate a very significant time inter-

in which these deposits may have been actually formed. This time embraces all of the three metallogenic stages of the Paleozoic, in contrast with the strictly limited time span for the contact-metasomatic deposits. We must take into account also the fact that, wherever the age of the deposits could be indicated paleontologically, by the limestones, age data are in a good agreement with the stratigraphic scale of the geologists (Mt. Karabash, the XIX Partsezd deposit, and others). This gives us confidence in the reliability of our determinations of the absolute age, in cases where there is no corresponding agreement between them and the geologic data.

Sericite rocks from two of the northernmost deposits, Kaban and Snogvardeiskoe, and from two of the Southern Ural deposits, Gai and Uchalinskoe, proved to be the most ancient ones belonging to the lower Paleozoic stage, in the Cambrian-Ordovician. Our figure for the Kaban deposit, 460 million years, agrees with the results of V. P. Vinogradov [4] based on his analysis of extensive geologic materials, with regard to the antiquity of this deposit, and with his conclusion that the Kaban deposit had been subjected to tectogenesis already in Caledonian times.

The Middle Paleozoic stage includes both the contact-metasomatic deposits and the chalcopyritic deposits of the Greenstone Belt in the Southern Urals: Levikha, Yasvinskoe, Yuzhno-kuznechikhinskoe, Mawksatinskoe, Karabash, Zyuzelskoe, and, in the Eastern Synclinal Zone, Sultanovskoe. As already stated [7], several pyritic deposits of the Middle Paleozoic stage may possibly be related to the contemporary contact-metasomatic deposits. We may be reminded here that a genetic relationship between the pyritic and the contact-metasomatic deposits was first established by A. N. Zavaritskii as early as 1929.

This is maintained correctly by A. D. Rakcheev [10], sericitization, in the generalized district, may recur many times, with different spans of intervening time. Absolute age data support this opinion. Alongside the sericite schists accompanying the Karabash-proper deposits, whose age is 350 million years, there exists a known sulfide mineralization in the same district, in serpentinites of a much later origin as shown by the age of the accompanying muscovite, which is 305 million years and in a good agreement with stratigraphic data.

The age of the pyritic deposits, as well as of the contact-metasomatic deposits, may be indicated not only by the associated metamorphic formations but also by the age of the vein rocks which is dependably correlated, as a rule, geologically with the mineralization. Determinations of the age by means of both types of rock provides a satisfactory check, exemplified by the Sultanovskoe deposit. The age of this deposit is 340 million years, by the quartz-sericite and by the Kersanite respectively, which means practically one and the same thing. The sericite rocks of the pyritic deposits belonging to the Upper Paleozoic metallogenic stage are probably Carboniferous; the Alekseevskoe, near Neivo-Rudyanka, and the Imeni XIX Partsezda, both in the Southern Urals. The formation of sericite schists at the former may be

related to the effects of the Verkh-Iset granitic intrusion of Harz age.

Assignment of this or that pyritic deposit to some definite metallogenic stage is highly tentative. It is possible that some deposits, particularly of the Middle Paleozoic stage, may prove to be much older, since it was proved, with the Krasnogvardeiskoe as an example, that there may be losses of argon from sericite schists [8]. This applies, first of all, to the Levikha deposit in the vicinity of which the age of a sericitized veined augitic porphyrite proved to be 420 million years [Table 2, sample No. 92].

The age of micaceous rocks in all pyritic deposits invariably almost coincides with the geologic age of the volcanogenic suites to whose metamorphism they owe their origin.* This, in turn, indicates an ancient age for a pyritic mineralization and its proximity, in time, to the age of the formation of its sedimentary-volcanic hosts. As in the case of the contact-metasomatic deposits, there was no appreciable time interval between the formation of sedimentary-volcanic suites, their metamorphism, deschistization, and mineralization.

Among the ore deposits associated with Harz intrusions, we determined the age of the Pyshma (copper-cobalt), the Bogomolovskoe (gold) and the Ilmen Complex (pegmatites). The Bogomolovskoe, notwithstanding its association with the Krasnouralsk group of pyritic deposits is of the same age as the Harz granites, 270 million years, as determined by the mica schist next to the vein, and is probably associated with the granites like all other vein deposits in this part of the Urals.

The Pyshma copper-cobalt deposit near Sverdlovsk is 250 million years old, by analysis of the biotite next to the ore, i.e., is close to the age of the Verkh-Iset granitic intrusive (265 million years), which is suggestive of their genetic relationship. The current view [5] to the effect that the Pyshma ores were derived from the gabbro magmas abundant in the ore field is not sustained.

The absolute age data for the Ilmenogorsk pegmatites agree very well with geologic ideas on the subject. The now proved Caledonian age of the muscovites from the Mt. Slyudyanyaya pegmatites is a new and interesting development. This is the first case of the discovery of pegmatites unrelated to the Harz intrusions.

We have merely touched upon a whole number of important problems in the data characterizing the absolute age of the principal type of ore deposits of the Urals. A further accumulation of evidence is essential.

*The Maukskoe deposit is an exception, on account of the discovery of Lower Proterozoic metamorphic rocks in its vicinity. This fact requires additional study, however.

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PROPORTIONS OF STRONTIUM AND CALCIUM
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Abstract

The strontium and calcium contents in rocks of the Lovozero massif range widely, from 0.008 to 1.75% of Sr and from 0.03 to 11.0% of Ca. A direct relation between the strontium and calcium contents in rocks has not been established. This is accounted for by the fact that strontium isomorphously replaces not only calcium but also potassium. Typical for the nepheline syenites of the Lovozero massif is a high strontium/calcium ratio. For rocks of the Lovozero massif the value of this ratio varies from 0.033 to 0.541, whereas for other rocks it is considerably less: for acid rocks, from 0.0167 to 0.023; for intermediate rocks, 0.0172; for basic rocks, 0.0065; and for ultrabasic rocks, 0.00035. The average strontium content in miascite rocks of the massif is higher than in apaitic rocks.

There is but little information in the geologic literature on the strontium content and on the strontium/calcium ratio of nepheline syenites. There are cited only the data of W. Noll [1], to the effect that nepheline syenites contain 0.14% SrO (average of 22 analyses), and A. Hansen's figure [2], 0.01% SrO (average of 34 analyses). K. K. Turen and J. L. Kulp [3], in a recently published report on geochemistry of strontium, give only two figures on strontium in nepheline syenites (gabbros): 0.146% Sr in one sample (the Oslo District, Norway) and 0.062% in the other one. The data on strontium for groups of rocks are somewhat more abundant. Some of them are cited in Table 1. Since the data on strontium in nepheline syenites are scarce and contradictory, we undertook to study the relative abundance of strontium and calcium in these rocks from the Lovozero massif, Kola Peninsula. As we know, this massif is a complex intrusive body, formed in several successive stages, and composed of the following rocks (beginning with the oldest):

1. A complex of uniformly-grained porphyroid, poikilitic, etc., nepheline syenites;
2. A complex of lujavrites, fojaïtes, and urtites;
3. A complex of eudialite lujavrites, with associated porphyroid lujavrites, tavites, and poikilitic sodalite syenites;
4. A complex of young dike rocks.

The bulk of the massif consists of the rocks of the Second Complex

Table 1. Strontium and Calcium Content in Rocks

Type of rock	% Sr	% Ca	Sr/Ca $\times 10^3$	Authority
Ultrabasic	2.7×10^{-3}	7.70	0.35	A. P. Vinogradov [4]
Basic	4.4×10^{-2}	6.72	6.55	A. P. Vinogradov [4]
Intermediate	8×10^{-2}	4.65	17.2	A. P. Vinogradov [4]
Acidic	3×10^{-2}	1.58	19.0	A. P. Vinogradov [4]
Sedimentary	4.5×10^{-2}	2.53	17.8	A. P. Vinogradov [4]
Nepheline syenites	1.2×10^{-1}	4.80	25	W. Noll [1]
Basaltic (average of 245 analyses)	4.65×10^{-2}	7.1	6.5	K. K. Turekian and J. L. Kulp [3]
Granites (average of 175 analyses)				
(a) 0.1 - 1.0% Ca	1×10^{-2}	0.6	16.7	K. K. Turekian and J. L. Kulp [3]
(b) 1.0 - 5% Ca	4.4×10^{-2}	1.9	23.0	K. K. Turekian and J. L. Kulp [3]
Crystalline schists	2.42×10^{-2}	3.1	7.9	K. K. Turekian and J. L. Kulp [3]

(lujavrites-fojaïtes-urtites by their composition) of which its lower part 900 to 1000 meters thick, is composed, and of the rocks of the Third Complex (eudialitic lujavrites) forming the 300- to 400-meter thick upper part.

The Lovozero massif contains 0.42 to 5.08% CaO, by chemical analysis.

The greatest quantities of strontium (5 and others) are found in the following minerals of the massif: 14.49 to 16.76% SrO in lamprophyllite; 33.60% in belovite; 5.50% in apatite; 7.40% in nordite; 2.00 to 3.42% in loparite; up to 1.42% in eudialite; 0.90% in erikite; 0.28% in shisolite; 0.01 to 0.08% in microcline; 0.06% in lovozerite.

The results of our determinations of strontium and calcium in rocks of the Lovozero massif are presented in Table 2.

Calcium and strontium were determined by the flame-spectrophotometric procedures. We employed the flame spectrophotometer with an air-acetylene burner and the double-glass monochromator D. M. The photoelectric circuit included a photo-amplifier FEU-17 and a rectifier VVS-1. The anode current of the photo-amplifier was measured by a mirror galvanometer with the sensitivity of 2×10^{-9} a./mm. The width of the intake and of the outgo slits for calcium was chosen at 0.08 to 0.12 mm for calcium and at 0.06 to 0.08 mm for strontium. The photometry was carried out by the 549.8 mm and 460.7 mm lines for calcium

Table 2. Strontium and Calcium Content of Rocks of the Lovozero Massif

Sample No.	Source	Rock	% SrO	% CaO	Sr/Ca x 10 ³
Rocks of the First Complex (miaskites)					
13	Mt. Alluaiv	Porphyroid nepheline syenite	0.25	2.57	115
16	Mt. Alluaiv	Poikilitic nepheline syenite with hydro-sodalite	0.18	1.60	130
19	Mt. Ninchurt	Uniformly grained nepheline syenite with biotite	0.33	2.30	169
26	Mt. Suoluaiv	Poikilitic nepheline syenite	0.22	2.10	124
Rocks of the Second Complex (agpaitic)					
4b	Mt. Karnasurt	Iolite-urtite with apatite	0.008	0.03	315
7	Mt. Alluaiv	Iolite-urtite	0.008	0.08	118
3	Mt. Karnasurt	Fojaite	0.12	0.55	258
4	Mt. Karnasurt	Fojaite	0.185	0.75	305
8	Mt. Alluaiv	Trachytoid fojaite	0.092	1.20	91
2	Mt. Parguaiv	Leucocratic lujavrite	0.06	1.25	57
35	Mt. Kuftnyn	Leucocratic lujavrite	0.12	1.30	109
4	Mt. Alluaiv	Melanocratic lujavrite	0.07	2.00	44
8	Mt. Karnasurt	Melanocratic lujavrite	0.085	1.80	56
6	Mt. Karnasurt	Mesocratic lujavrite	0.055	1.70	39
8	Mt. Karnasurt	Amphibolite lujavrite	0.087	0.86	49
4	Mt. Alluaiv	Lujavrite with loparite	0.12	2.60	541
2	Mt. Alluaiv	Urtite with loparite	0.52	2.00	307
8	Mt. Alluaiv	Urtite with apatite and loparite	1.75	11.00	188
7	Mt. Karnasurt	Maliniite with loparite	0.69	2.30	355
Rocks of the Third Complex (agpaitic)					
5	Mt. Alluaiv	Eudialitic lujavrite	0.20	2.22	108
9	Mt. Alluaiv	Eudialitic lujavrite	0.28	1.55	214
6	Mt. Alluaiv	Porphyroid juvite with loparite	0.145	1.00	171

Table 2 (Continued)

Sample No.	Source	Rock	% SrO	% CaO	Sr/Ca x 10
Rocks of the Third Complex (agpaitic) (continued)					
263	Mt. Karnasurt	Porphyroid lovozeritic lujavrite	0.39	2.00	230
106	Mt. Vavnbéd	Porphyroid lovozeritic lujavrite with lomonosovite	0.29	1.20	286
XXI	Mt. Flora	Porphyroid lujavrite with murmanite	0.065	0.70	110
141	Chinglusuai River Valley	Poikilitic sodalitic syenite	0.040	1.40	34
430	Tavaiok Pass	Tavite	0.040	1.45	33
266	Tulbnyunnuai River Valley	Poikilitic sodalitic syenite	0.040	0.85	56

and strontium respectively. The background was measured at both sides of the lines, and its averages were used. Sensitivity of the instrument was not below 0.05 γ /ml, with the galvanometer's deflection by one division of the scale.

Procedure: 0.5 gram aliquot of a finely pulverized rock, in a platinum disk, was wetted with water and treated with 15 to 20 mls of hydrofluoric and 10 to 15 mls hydrochloric acid. The dry residue was ignited at 400 to 450°C and dissolved in 10 mls of 1:1 hydrochloric acid. The sesquioxides were precipitated with 1:1 ammonia, CO₂-free, by neutralizing the 80 to 90 mls solution to the methyl red end point. The solution containing the precipitate was made up to 100 mls and filtered. A part of the filtrate was analyzed photometrically. A modified procedure was used for samples containing less than 0.05% SrO or CaO.

After precipitation of the sesquioxides, the precipitate was filtered off and washed with 0.2% aqueous ammonium nitrate and the filtrate was evaporated, transferred into a 25 mls flask, made up to the mark and examined photometrically.

Exact solutions of calcium and strontium were prepared by dissolving their carbonates in the minimum quantity of hydrochloric acid. The photometric standards, containing 3 grams of ammonium chloride per 100 mls, were prepared with 0, 0.5, 1.0, 2.0, 4.0*, 6.0, 10, 15, 20, 30, 40 γ /ml SrO and 0.2, 5, 10, 15, 25, 40, 60, 90 γ /ml CaO, with additions of sodium and potassium chlorides in amounts the same as are found in the samples.

*"1.0" in the original; a misprint; corrected - VPS.

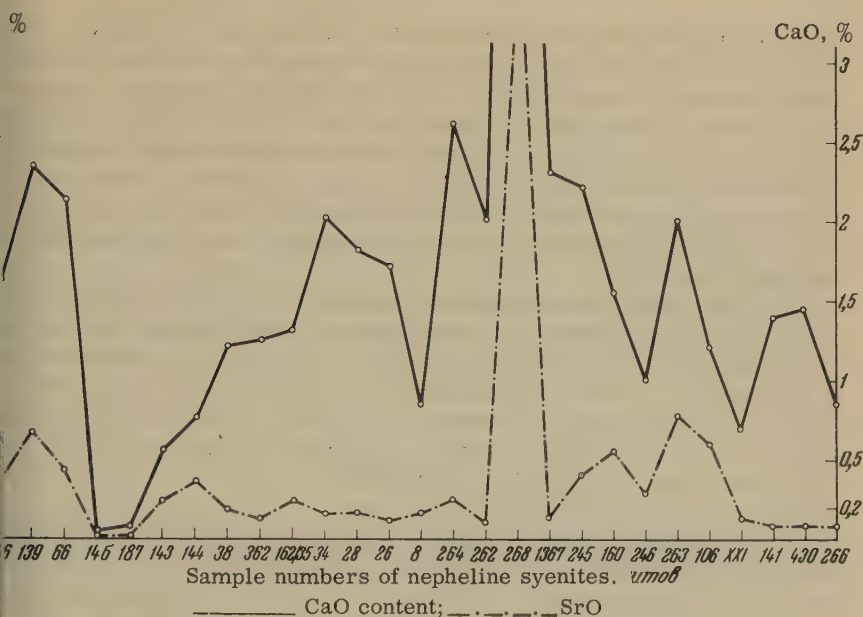


Fig. 1. Sr and Ca content of rocks of the Lovozero Massif.

the "method of additions"*** was used for samples containing less than 0.01% SrO.

The data reported in Table 2 show that the contents of both strontium and calcium in the Lovozero massif's rocks vary within a wide range: from 0.008% SrO and 0.03 to 11% CaO. There is no correlation between the amounts of strontium and calcium in these rocks (Fig. 1), although the smallest quantities of SrO (0.008%) were found in the rocks that are very low also in CaO (0.03 to 0.07%), whereas the maximum of SrO (1.75%) appears in a calcium-rich rock (11% CaO). The strontium content is characteristic of the rocks that are high in calcium-rich minerals, namely, of iolite-urtites, which are chiefly nepheline, as well as of rocks containing large amounts of sodalite (e.g., poikilitic sodalitic syenite).

The strontium-calcium ratio in the rocks of the massif (Table 2) is determined at 0.033 to 0.541. This ratio varies most significantly (from 0.033 to 0.541) in rocks of the Second Complex (lujavrites, fojaite, urtites), where the quantitative proportions of the rock-forming minerals are subject to marked fluctuations.

The absence of a direct interdependence between the contents of strontium and calcium content and the resulting wide variations in the strontium-calcium ratios may be explained probably by isomorphous substitutions of strontium not only for calcium but also for potassium (e.g., in feldspars and in other minerals), because the size of their ions is similar; i.e., adding known amounts of the standard to the test solution, VPS.

not too different from each other (Sr^{2+} 1.27Å; Ca^{2+} 1.06Å; K^+ 1.33Å).

The isomorphous substitution of strontium for calcium in minerals of the Lovozero massif is very common, and the ordinarily high concentrations of strontium are found only in minerals high in calcium. Strontium is characterized by its paragenesis not only with calcium but also with sodium, in minerals genetically related to the agpaite rocks of the Second and of the Third Complex (Table 3). All minerals listed in Table 3, with the exception of apatite, are characteristic for agpaite rocks.

The possibility of isomorphous replacement of potassium by strontium in potassium feldspars is confirmed by detections of strontium in these minerals. For example, the Lovozero microcline contains 0.01 to 0.08% SrO (V. A. Moleva, Analyst). W. Noll also [1] reports the presence of strontium in potassium feldspars from nepheline syenites. According to his findings, there is 0.2% SrO in a Na microcline from lardalite (Lave, southern Norway), whereas nepheline from the same rock has 0.01 to 0.001% SrO.

The Lovozero massif, as a whole, is undoubtedly high in strontium and is characterized by very high strontium-calcium ratios, as is shown by the data reported in Table 2. The First, Second, and Third Complexes contain 0.24, 0.098, and 0.22% SrO respectively, on the average. The rocks of the First Complex have not more than 1% of the total volume of the massif as their share; volumes allotted to the Second and the Third Complex are 75% and 24% respectively. Consequently, the total (weighted mean - VPS) SrO content of the massif is about 0.12%. This is higher than the strontium content of magmatic rocks (Table 1). Nepheline syenites of the Lovozero massif differ markedly from the rest of the magmatic rocks (basic, intermediate, acidic) by their high strontium-calcium ratio. Although this ratio varies from 0.33 to 0.541 in the Lovozero rocks, it is significantly lower for the others: 0.016 to 0.023, 0.017, 0.0065, 0.00035, for acidic, intermediate, basic, and ultrabasic rocks respectively (Table 2).

Various poikilitic syenites are encountered in the Lovozero massif. They were classified as members of one and the same intrusive phase by several investigators. However, analysis of the results shown in Table 2 indicates an essential difference between the poikilitic sodalite syenites and the other poikilitic syenites of the massif, with respect

Table 3

Mineral	% SrO	% CaO	% Na ₂ O
Lamprophyllite	14.49 - 16.76	1.20 - 1.72	10.83 - 12.70
Belovite	33.60	5.23	3.60
Apatite	5.50	48.80	-
Nordite	7.40	4.46	11.70
Loparite	2.0 - 3.4	3.80 - 5.46	8.9
Eudialite	up to 1.42	7 - 11	11.16
Erikite	0.90	1.57 - 1.81	1.05

th to strontium content and to strontium-calcium ratio. This circumstance is one of the proofs that the poikilitic sodalite syenites are not contemporaneous with poikilitic nepheline syenites. We classify the latter as members of the First Complex and the poikilitic sodalite syenites as members of the Third Complex.

We must remark, in conclusion, that the average strontium content in miaskites in the First Complex of the Lovozero massif is higher than in the agpaite rocks in the Second and in the Third Complex. This fact merits a high degree of attention. The former belief was to the effect that there is less strontium in the miaskites than in agpaites, in the Lovozero massif, because the latter are relatively more abundant than the strontium-bearing minerals (lamprophyllite, loparite, eudialite, and others).

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ON Nb/Ta RATIOS IN SOME MINERALS FROM IGNEOUS AND METASOMATIC ROCKS

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Abstract

The Nb/Ta ratio has been determined in 52 Ta-Nb minerals from the Eastern Tuva area. The following minerals have been studied: columbite, fergusonite, euxenite, pyrochlore and microlite. It has been shown that the Zr/Hf ratio depends in zircons on the alkalinity of rocks and the genetic peculiarities of the magmatic and postmagmatic processes; the Nb/Ta ratio in the minerals studied is chiefly connected with the general age evolution of the magma in time. During the development of magmatism in the area a relative Nb accumulation in complexes of a younger age developed.

Genetic factors in the range of rock complexes of similar age have the same influence upon the Nb/Ta ratio as in the case of Zr and Hf, which, however, is displayed to a lesser degree. A strong change in the Nb/Ta ratio is only observed in euxenites.

Proportions of certain rare elements, in minerals and rocks, may be utilized as sensitive indicators of geologic processes, if these elements resemble each other in their chemical properties. This was shown to be the case for the rare earths and for Zr and Hf in a series of our reports [1, 2, 3, 4]. It is especially interesting, for that reason, to inquire now into the possibilities presenting themselves in connection with the use of ratios between suitable groups of elements as geochemical indicators of geologic processes. Such studies may be conducted more conveniently, it appears, in one region, a test area, where a wide variety of magmatic complexes of different ages and petrography are united through a common rare-metal metallogeny. By studying the behavior of certain geochemical pairs of elements or groups of elements within the confines of a unified region of this type, we may ascertain the factors which exert a decisive influence on the magnitudes of the various ratios and on the range of their fluctuations, while they regulate migrations and accumulations of individual elements. We had already noted a parallelism between Zr-Hf and the rare earths, in a magmatic process [4]. This study is concerned with relationships governing the Nb-Ta ratios in some minerals of magmatic and metasomatic rocks and with comparisons between the Nb-Ta and the Zr-Hf ratios. Whereas Zr and Hf are found almost entirely in zircons formed in rocks of a highly variable composition and within a wide range of mineral-forming

environments, Nb and Ta form several species of minerals, each of which is associated only with a certain range of petrographic compositions. This consideration has made it essential for us to examine a series of tantalum-niobium minerals and, first of all, columbite, fergusonite, euxenite, pyrochlore, and microlite.

The Eastern Tuva district is especially well suited as a test area for studies of the geochemical history of Nb-Ta, Zr-Hf, the rare earths, Th-U, during the evolution of magmatic and post-magmatic processes. The zircons from different rock complexes of this district have already been investigated in our earlier work [3].

CHARACTERISTICS OF GEOLOGIC ENVIRONMENTS OF TANTALUM AND NIOBIUM MINERALS

The southern and the eastern sections of the Eastern Tuva district are composed of Upper Proterozoic and Sinian terrigenous and carbonate rocks. Cambrian effusive-sedimentary rocks make their appearance to the north and to the west of the Upper Proterozoic-Sinian formations and are succeeded farther to the northwest by Ordovician, Silurian, and Lower Devonian effusive-sedimentary bodies.

Upper Proterozoic granites and granodiorites (the Sayan Complex) and Lower Cambrian ultrabasic rocks (the Aktovrak Complex) are the oldest magmatic rocks of Eastern Tuva; they are not extensive in their distribution. The bulk of the intrusives in Eastern Tuva is of the Upper Paleozoic (the Tannuola Complex, Pre-Ordovician) and Middle Devonian (the Syutkhol Complex). The first one of these complexes is represented by various intrusions, from gabbro to granite, with a prevalence of the intermediate rocks; the second one by granites, diorites, syenites and syenites. Most of the intrusions of the two complexes occur within Paleozoic effusive-sedimentary rocks, although many of their smaller massifs are found also within the belt of the Upper Proterozoic sedimentary-metamorphic rocks.

The alkalic complex, represented by many relatively small intrusions, ranging from urtites to alkalic granitoids in composition, appears to be associated with the Middle Devonian granitoids. All of the known alkalic massifs are in Upper-Paleozoic-Sinian formations. The stages in the evolution of the alkali complex are definitely recognizable at this time: the ancient alkalic phase, represented by nepheline and alkalic syenites, and the sub-alkalic stage. Alkalic and nepheline syenites and alkalic granitoids of the second stage transect rocks of the first stage.

Rare-metal occurrences, including tantalo-niobates, in Eastern Tuva are found in the vast majority of the cases associated with the alkalic rocks. Although some of them are known to be associated with intrusions older than the alkalic rocks at several sites in Eastern Tuva, it is difficult to assign them definitely to a particular intrusive. The most probable association, in this respect, is with the Middle Paleozoic Complex (Bren,

Syutkhol) which preceded the alkalic intrusions and was probably the original hearth for the alkalic magmas. At the same time there is no exclusion of the possibility that some of the rare-metal occurrences, such as that at Khusuingol, are related to the more ancient Tannuola granites.

The present study included Nb and Ta minerals from every one of the known principal sources in the area. Most of the specimens were collected by the Tuva Field Party of The V. I. Vernadskii Memorial Institute of Geochemistry and Analytical Chemistry, Academy of Sciences of the USSR; one specimen was received from V. I. Kudarin, three from Yu. V. Makhin, two from I. A. Nechaeva, to all of whom the authors are greatly indebted.

Brief descriptions of the massifs from which specimens were examined in the present study are presently to be given, with the exception of the Erzin, the Aksug, the Orgutin, and the Balyktygkhem massifs already described in the earlier publication [3]. Characteristics of the specimens themselves are reported in Table 1.

The Terekhol Massif consists chiefly of ordinary foyaites and miaskites succeeded by alkalic and even by quartz-syenites in the northern and the northeastern sections of the intrusions. Khibinite-like varieties, with astrophyllite and rinkolite, appear in the eastern endomorph zone next to the gabbroids of the Tannuola Complex. All of the rocks belong apparently to the first stage. Accumulations of pyrochlore are found in areas of autometasomatic albitization as well as in the alkalic pegmatites.

The Agash Complex is a rounded stock composed chiefly of alkalic and nepheline-bearing syenites of the stage of the alkalic intrusion. Leucocratic miaskites and quartz syenites are present in subordinate quantities. All of these rocks grade into one another and may be regarded as different facies of one single intrusion. Fergusonite with zircon and, more rarely, with thorianite, is found in albitized and microclinized sections of the alkalic syenites, commonly associated with the contacts with xenoliths in the limestones.

The Dugdin Massif is an intricate intrusive complex involving rocks of the first and second intrusive stages occupying extensive areas. Its characteristic feature is a close position to nepheline syenites, alkalic syenites that pierce them, and granitoids of the second stage. There are several occurrences of rare metals within the massif, although not a single one of them is directly associated with the nepheline syenites. Accumulations of rare metals are found chiefly in veins and pegmatites in auto-metasomatic rocks, and in the exomorphic zones between metasomatites and alkalic granitoids. Superimposition of the ore-bearing vein and metasomatic formations of the second stage on mariupolites of the first stage is observed in several cases.

From petrographic indications, the following rocks are referred to the alkalic granitoids of the second stage: leucocratic alkalic biotite granites of the Milzei (No. 37, sample No. 121); the Uzun-Taiga pegmatitic veins (No. 38, sample No. 3000). The latter are commonly

Table 1. Characteristics of Samples and the Results of Their X-Ray Spectrographic Analysis

Sample No.	Mineral	Source	% Nb	% Ta	Nb/Ta
ERZIN MASSIF					
UT-61	Columbite	Quartz-feldspar albitized pegmatoid vein	51	6.1	8
UT-53/1	Columbite	Silicified hydromuscovite rock from mylonitized zone in alkalic granite-porphyrries	48	4.4	11
UT-51/1	Columbite	Silicified hydromuscovite albitite	57	5.2	11
UT-58	Columbite	Strongly albitized riebeckite granite	16	0.9	14.5
UT-63	Columbite	Albitized riebeckite granite	26	1.5	17.5
UT-57	Columbite	Albitized leucocratic alkalic granite	20	1.2	18
UT-50/1	Columbite	Albitized silicified leucocratic granite porphyry	45	2.1	22
UT-52/1	Columbite	Albitized hydromuscovitized leucocratic alkalic granite-porphyry	57	8.0	29*
UT-050	Columbite	Quartz vein in leucocratic alkalic granites	41	1.7	24
AKSUG MASSIF					
A-112/8	Euxenite	Albitized quartz syenite	13	0.9	14.5
A-103/31	Euxenite	Riebeckite-albite "Schlieren" in albitized quartz syenite	26	1.2	22
A-103/4	Euxenite	Riebeckite-albite "schlieren" in albitized quartz syenite	27	1.15	23
A-105/11	Euxenite	Albitized silicified bostonite	34	1.0	34
A-10/46	Euxenite	Riebeckite-albite-citrolite vein	27	0.35	80
A-103/3	Euxenite	Riebeckite-albite-citrolite vein	25	0.25	100
ORUGTIN MASSIF †					
0120	Pyrochlore	Coarse-grained biotitic nepheline-cancrinite miaskite	25	3.4	7.4
0117	Pyrochlore	Microclinized nepheline biotite miaskite	28	2.4	11.5
0121	Pyrochlore	Albitized hornblende-biotite pulaskite; Karevaya facies	34	2.9	21.0
BALYKTYGHEM MASSIF					
KA-8/1	Aeschynite	Albitized microcline-nepheline mariupolite	10	0.7	12
KA-18	Aeschynite	Albitized bostonite	6.8	0.96	17*
TEREKHOL MASSIF					
TKh-38	Pyrochlore	Albitized section of foyaites. Aegirine mariupolite	13	0.9	14.5
TKh-30	Pyrochlore	Albitized silicified syenite of riebeckite-aegirine quartz of canadite type, within sahlband of alkalic pegmatite	26	1.8	14.5
AGASH MASSIF					
AG-152	Fergusonite	Biotite canadite (plagioclase-microcline) strongly microclinized	29	2.9	10
AG-46	Fergusonite	Microclinized and albitized alkalic syenite with biotite, riebeckite, aegirine, fluorite, and carbonate	32	1.9	17
AG-154	Fergusonite	Microclinized and albitized biotite alkalic syenite. Locally weakly silicified	33	1.3	25
AG-42	Fergusonite	Microclinized and albitized biotite alkalic syenite. Locally weakly silicified	25	1.0	25
AG-151	Fergusonite	Weakly microclinized alkalic syenite	32	1.0	32

No.	Sample No.	Mineral	Source	% Nb	% Ta	Nb/Ta
DUGDIN MASSIF						
28	DG-0143	Pyrochlore	Microclinized and albitized mariupolite with zircon, pyrochlore, and apatite †	27	2.7	10
29	DG-131	Pyrochlore	Aegirinic-microclitic, strongly albitized rock with carbonate and fluorite; originated by replacement of gabbroid rocks	31	2.6	11
30	DG-126	Pyrochlore	Riebeckite-quartz vein rock with relics of microcline-perthite, magnetite, zircon, and pyrochlore	34	2.1	16
31	26	Pyrochlore	Riebeckite-quartz vein rock with relics of microcline-perthite, magnetite, zircon, and pyrochlore	30	2.0	15
32	DG-125	Pyrochlore	Riebeckite-microcline pegmatoid vein with magnetite	30	1.7	18
33	DG-128	Pyrochlore	Pegmatoid schlieren in alkalic granitoids. Albitized and silicified aegirinitic granosyenite	35	1.9	18
34	326	Pyrochlore	Pegmatoid alkalic aegirinitic granite, high in quartz	18	1.0	18
35	438	Pyrochlore	Aegirinitic albitite after melanocratic alkalic aegirinitic syenite	20	1.0	20
36	296	Fergusonite	Quartz-magnetitic metasomatic rock with fergusonite, allanite, and zircon; formed after gabbro	25	2.4	10
MILZEI MASSIF						
37	121	Euxenite	Alkalic granite	13	2.3	5
UZUNTAIGA MASSIF						
38	3000	Euxenite	Alkalic pegmatite	15	1.1	13
ZHINKHEM MASSIF						
39	779	Columbite	Alkalic pegmatite	45	2.5	18
BAYANKOL MASSIF						
40	BYa-70/3	Columbite	Amazonitic pegmatite	52	11	4
41	BYa-671	Fergusonite	Amazonitic pegmatite	22	6.4	3
KHUSINGOL MASSIF						
42	T-114	Columbite	Leucocratic pegmatoid quartz-feldspar vein with muscovite and garnet	32	2.0	16
43	T-113	Columbite	Leucocratic garnet-bearing pegmatoid granite, low in quartz	34	4.5	7
44	T-100	Columbite	Spodumene albitized pegmatite	35	9	3
45	T-101	Fergusonite	Spodumene, more or less albitized pegmatites	28	2.8	10
46	T-102	Fergusonite	Spodumene, more or less albitized pegmatites	29	5.7	5
47	T-103	Fergusonite	Spodumene, more or less albitized pegmatites	31	6.0	5
48	T-109	Fergusonite	Spodumene, more or less albitized pegmatites	22	4.0	5
49	T-101	Microcline	Spodumene, more or less albitized pegmatites	17	13	1
50	T-102	Microcline	Spodumene, more or less albitized pegmatites	22	17	1
51	T-109	Microcline	Spodumene, more or less albitized pegmatites	23	13	1
52	T-108	Fergusonite	Pegmatoid leucocratic albitized granite	28	4.4	6
53	T-108	Microcline	Pegmatoid leucocratic albitized granite	15	28	0

* If % Nb and % Ta, Nos. 8 and 20, are reported correctly in the original, the Nb/Ta ratios should be 7.1 and 7.1 respectively and not 29 and 17 as shown in the last column of the table. VPS.

† Rocks of the Orugtin and of the Balyktyghem Intrusions belong to the first phase of the Alkalic Complex rocks of the Erzin and the Aksug to the second phase.

‡ Sample DG-0143 is placed tentatively in the nepheline syenite field, in the diagram (Fig. 3), because of the presence of pyrochlore in the nepheline rock.

presented by silicified alkalic-limestone syenites of the larvikite-amazonite type resembling the Aksug rocks (Table 1). We must remember, however, that there is no direct geologic evidence for referring these rocks, especially the Milzei granites, to the second stage. Tantaloniobates are represented by euxenite in both instances.

The various vein granitoids from the headwaters of the Zhin-Khem river may be referred to the second stage with a sufficient confidence, on the basis of their petrographic composition and their geologic position. Columbite (Na 39, sample No. 779) was isolated from a leucocratalbitized microcline-quartz vein where it is found together with zircon and monazite.

The niobium-tantalum mineralization related to granites older than the alkalic complex is represented by two sections: Bayankol (sample index BYa) and Khusuingol (Sample index T). The Bayankol mineralization is a stock of amazonite pegmatites containing segregations of columbite, fergusonite, and a peculiar phosphate-silicate of rare members of the cheralite type [5]. Leucocratic feldspathic pegmatites with garnet, as well as spodumene pegmatites, are well developed in the Khusuingol section. They contain also cassiterite, beryl, and monazite in paragenetic associations with columbite, fergusonite, and microcline.

CHARACTERISTICS OF MINERALS

As stated in Table 1, we examined the following minerals in the present study: columbite, fergusonite, euxenite, pyrochlore, and microcline. All of the minerals analyzed by us were conclusively identified by optical, spectrographic, microchemical methods and by X-ray analysis. The latter procedure was applied to ignited samples, in the determination of metamict varieties of the minerals.

Columbites. Theoretically, a pure niobium columbite contains 22.9% Nb; columbite with the Nb/Ta ratio of 1:1, 21.9% Nb and 42.5% Ta. The Nb content of our samples ranged from 16 to 51% and their Ta content from 0.9 to 11% (Table 1). The Nb and Ta content, where it is below the theoretical one, is explained partly by poikilitic ingrowths of the rock-forming minerals, partly by admixtures of ore minerals, especially hematite, inseparable from the fine fractions of columbite in the preparation of the sample.* Mineralogic studies and spectrographic analysis show absence of the other Nb and Ta minerals in the columbite sections. We are justified, therefore, in discussing the experimentally obtained Nb/Ta ratios.

Fergusonites. By its theoretical formula, pure fergusonite contains 33.3% Nb and pure formantite 54.2% Ta. The range of variation for Nb, in our fergusonites, was 22 to 33% and the range for Ta 1.0 to 6.4%, which agreed very well with both theoretical and natural compositions.

The Nb content of samples 3 and 8 (Table 1), up to 57%, is due to errors in the analysis.

The somewhat abnormally low results, in some isolated cases, may be explained by admixtures of Ti and by presence of hydrated crusts.

Euxenite belongs to the group of tantalum-titanium-niobates having an extremely variable and unstable composition. The percentage of Nb in natural specimens ranges from 14 to 20, on the average, rising in some to 28% [6]. The niobium content of our euxenites is 13 to 27%. The higher concentration in the No. 13 sample may be due possibly to its resemblance to fergusonite in its composition.

Pyrochlore. Natural pyrochlores contain 24 to 44% Nb [6]. Our pyrochlores fall within this range; 25 to 30% Nb. The low results in a few samples may be due to contamination of the very fine fractions chiefly by sphene. Samples from the Balyktyghem Massif are represented by aeschynite.

Microlite. This name was given provisionally because of its high Ta content. Natural pyrochlores, with Nb/Ta ratios analogous to ours, contain about 21% Nb and 8 to 24% Ta [6]. Our microlites are also in the same range: 17 to 25% Nb and 11 to 12% Ta.

Before we pass to a discussion of the analytical results on the Nb-Ta ratios in tantalum-niobates, we must take into account certain special features of their distribution.

Whereas Zr and Hf are accumulated almost entirely in zircon, which is found in rocks of any composition (with the exception of strongly agpaite rocks), Nb and Ta form series of mineral species each of which is associated only with a certain definite range of petrographic compositions. Moreover zircon is formed during all of the mineral-forming stages, from the magmatic to the relatively low-temperature hydrothermal, functioning, in this respect, as a "polygenetic" mineral. The formation of Nb and Ta minerals, on the contrary, is confined to the range of the pegmatitic and the high-temperature hydrothermal-metasomatic processes. Columbite, pyrochlore, euxenite, found as accessory admixtures in magmatic rocks (Erzin, Khusuingol, Orugty, Milzei, Dugda), on closer study, prove to be associated with high-temperature diffusive autometasomatic process. Consequently, every one of these mineral species may serve as a geochemical indicator of the relatively narrow groups of pegmatitic and post-pegmatitic rocks related to an intrusion of a certain definite composition. Indeed, as is evident from Table 1, different mineral species are found in the rocks of different composition, as follows: columbite - only in granitoids; the rare-earth tantalum-niobates, fergusonite and euxenite - are characteristic for sub-alkalic rocks, of the alkalic and quartz syenite type, and are known to be found also in albitized alkalic-enriched granitic pegmatites (the Khusuingol lithium pegmatites, the Bayankol and the Uzun-Taiga microcline-albite pegmatites); microlite is found only in the Khusuingol lithium pegmatites.

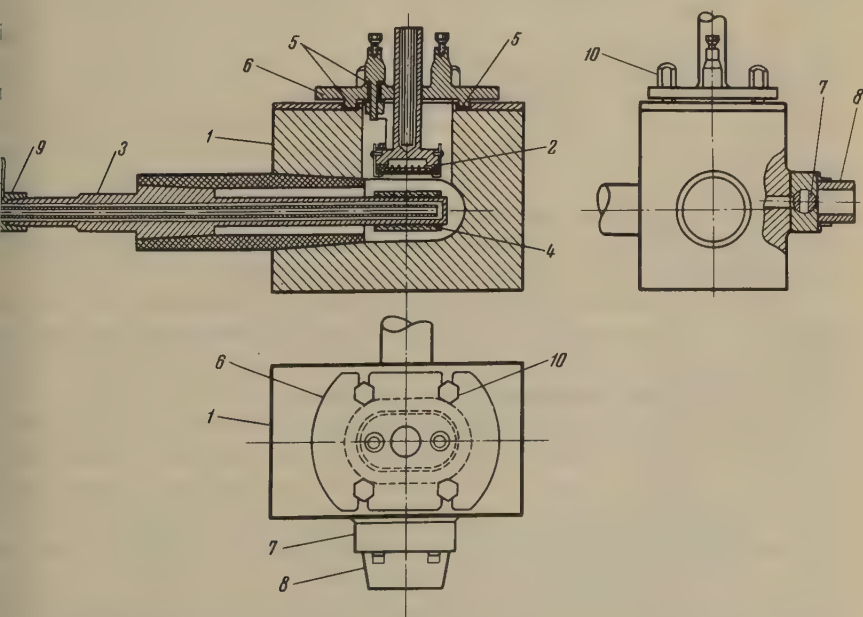
Characteristically within the boundaries of this latter mineralized section, columbite is associated with normal pegmatites and with pegmatoid granites containing appreciable quantities of primary oligoclase and containing no perthite, whereas fergusonite and microlite are

developed only in the albitized spodumene pegmatites. Pyrochlore is the most characteristic mineral of nepheline syenites and is found significantly more rarely in alkalic or in quartz syenites and in alkalic granitoids. In such cases, moreover, the sub-alkalic rocks are most closely related to the nepheline syenites, spatially and genetically. Thus, in the Terekhol and in the Orugty, the alkalic and quartz syenites are facies of the nepheline syenites; in the Dugda, pyrochlore is found in uranopolites and in albitites which originated under the influence of alkalic granitoids, as well as in the granitoids themselves, which are in contact with the nepheline-bearing rocks. We will not consider the causes of the formation of different mineral species, inasmuch as this problem has an independent significance.

QUANTITATIVE X-RAY SPECTROGRAPHIC METHODS FOR DETERMINATION OF Nb AND Ta IN MINERALS

The X-ray spectrographic analysis of minerals is based on the primary excitation of the spectra, in a short-wave X-ray spectrograph, to the point of the "penetration".

The X-ray tube, represented in Figure 1, served to improve reliability and speed of the analysis. The anode of the tube was equipped



1. Diagram of X-ray spectrographic tube: 1—body; 2—cathode; 3—anode, removable tip; 4 and 5—vacuum packing; 6—top lid of the tube; 7—screen for the fixation of the beginning and of the end of the exposure; 8—film diaphragm; 9—water-cooler muffle, for inclusion in the circuit; 10—flap-bolts of the upper

with a removable 4-facet tip; test materials and the standard mixture were placed onto every one of the four facets. They could be moved successively under the cathode beam, by turning the anode on its bearings, by 90° , without any disturbance of the vacuum in the tube. The water-cooled jackets stay fixed during the revolutions.

As we know [7], intensity of the X-rays and their response to the composition of the sample depend on the angle at which the anode mirror is set with respect to the axis of the X-ray beam. This relationship is not the same for lines of different wave length. In our case, the dependence showed to a greater extent for the long-wave tantalum line. Experience shows that the optimum angle α (between the anode mirror and the axis of the X-ray beam) is 30° , in the analysis for Nb and Ta. We made the appropriate markings on the anode and on the isolator, so as to facilitate maintenance of the constancy of this angle. In order to avoid displacements of the focus-spot on the anode, the position of the incandescent thread heating the oxide cathode was firmly fixed. The length of the focus of the electronic beam was maintained by means of Γ -shaped brickettes, focusing guides, that could be so arranged as to produce focuses of different length. A special cylindrical screen was used in the control of the beginning and of the termination of the exposures. Intensity of the thermo-electronic emission of the cathode and its stability in time were increased by the following oxide mixture: BaO:SrO:CaO = 50:45:5 (by weight). This combination was mixed thoroughly prior to its ignition at 1000°C [8]. In order to assure a rapid and a complete cleansing of the inner space of the tube, the tube was rid of every acute angle, and its walls were carefully smoothed and polished. Rubbing with a piece of cotton soaked in benzene was sufficient for the cleaning of the polished surface. The tube could be dismantled rapidly, as it had semidetachable bolts. Evacuation of the tube, to a high vacuum, was carried out by a single pumping apparatus, with the appropriate valves, connecting the vacuum system with the cavity of the tube by a single wide channel.

Niobium and tantalum were determined quantitatively, by the $K\alpha_1$ and the $L\alpha_1$ lines respectively (corresponding to the second and to the first orders of the reflection), by comparing their intensities in the test minerals with appropriate standard mixtures.

Three samples and one appropriate standard were placed on the grooved surfaces of the removable tip of the anode and packed densely in certain definite areas of the surfaces whose size was somewhat larger than the size of the focus-spot. Both the samples and the standard were then saturated with a measured quantity (1 or 2 drops) of B-2 glue, diluted to the required consistency, and were dried for 10 to 15 minutes at 120 to 150°C . The glue serves to prevent falling of particles from the anode, under the influence of the field, from one surface onto another, or onto the incandescent thread of the cathode, protecting the oxide mixture from a rapid decomposition. As has been shown by controlled experiments, in the sample-placement procedure here employed, after 100% exposure of an element from one of the facets,

the adjoining facets remain contaminated within the limits of sensitivity of the method (0.05%).

Samples of the minerals are analyzed, with the X-ray beam at 15 m.a. and 40 kv, in 5-15 minute exposures. In order to avoid overexposures of the lines whose content was appreciably higher than the content of Ta, as a rule, intensities of $K\alpha_{1,2}$ niobium lines were weakened by means of an aluminum absorber, 1 mm thick, placed across the path of the beam. The standard mixture was exposed before and after exposures of the samples and of the five spectra were recorded in one spectrogram, on Agfa-Laue type of the X-ray films. Methol-hydroquinone was used as the developer; time of the development: 8 minutes at 20°C. Densities of the spectrogram were determined photometrically by the MF-2 photometer.

A sensitometric emulsion curve was employed in calculations of the densities. However, when increases in densities of the lines do not exceed 0.05 to 0.07, as in the analyses of materials high in the elements of our interest, by short-time exposures, the calculations are made easier by the nomograms (Fig. 2) based on the sensitometric emulsion curve. The lines shown in Figure 2 represent the dependence of the relative densities of test element lines from the corresponding density-change ratios (δ_1/δ_2), with the δ_1 —the increase in the density of the denser line—as the parameter.

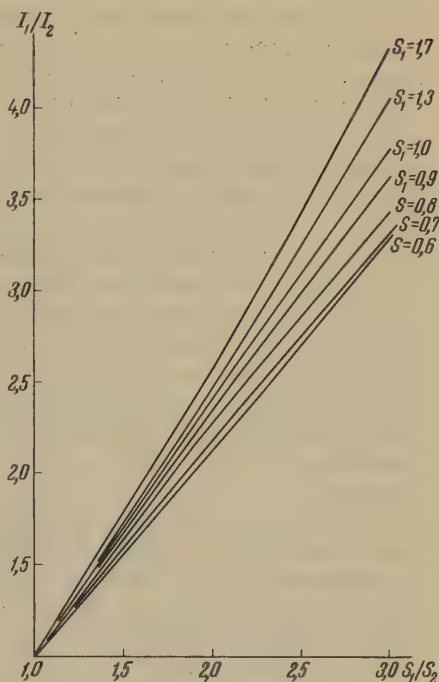


Fig. 2. Nomograms for calculation of the ratios of line intensities.

EXPERIMENTAL DATA ON DISTRIBUTION OF Nb AND Ta IN MINERALS AND THEIR DISCUSSION

The experimental data on the quantities of Nb and Ta in minerals shown in Table 1 and are represented diagrammatically in Figure 1. As one may see, the Nb/Ta ratio in different minerals fluctuates within the following limits: A consideration of these figures enables one to draw the following conclusions:

(a) All of the ratios, with the exception of those for the microlites extremely rich in tantalum and two of the euxenites, are within the range of 3.5 to 34 which is substantially different from the Zr/Hf range (14 to 217) in zircons [3].

(b) The range of variation of the Nb/Ta ratio is about the same for columbites and fergusonites from granitic rocks. The range of variation of this ratio is likewise comparable, in the instance of columbites, fergusonites, euxenites, and pyrochlores in sub-alkalic rocks.

(c) The Nb/Ta ratios in pyrochlores from nepheline syenites are intermediate between these ratios in the minerals from granites and from sub-alkalic rocks, which is an expression of the age and not of the petrochemical successions of nepheline syenites.

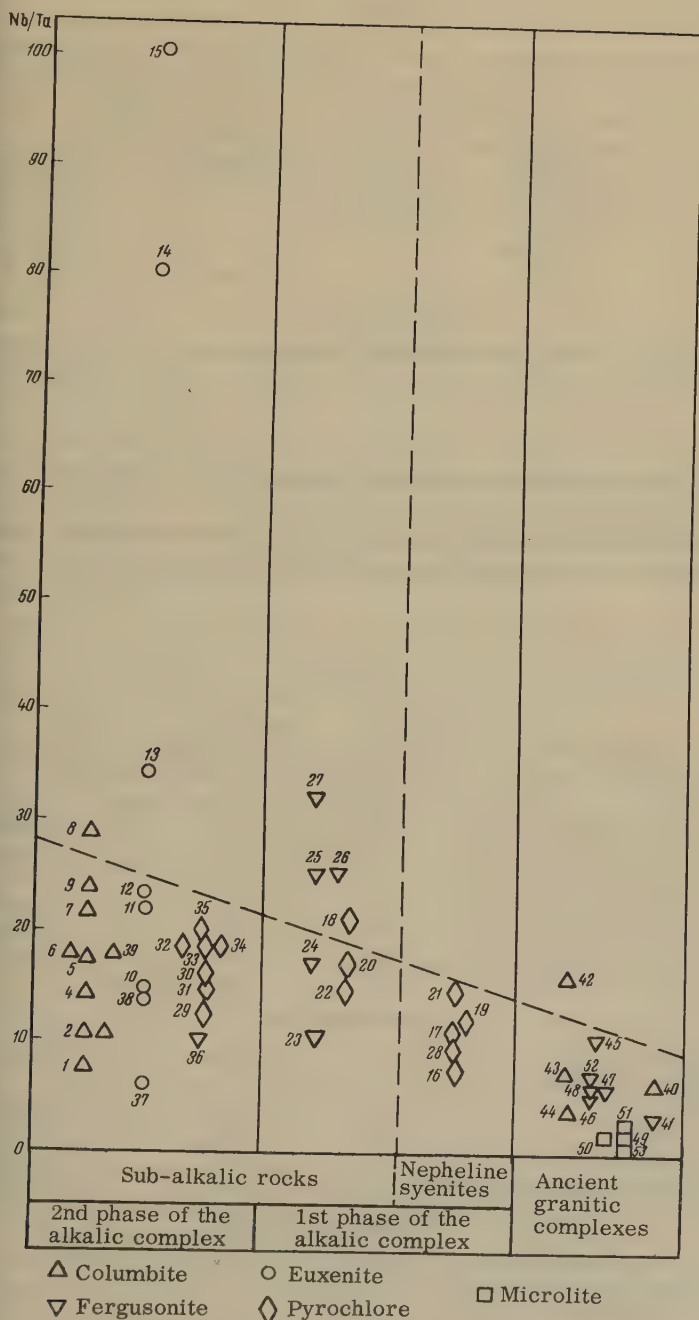
(d) On the whole, the Nb/Ta ratio, in all of the mineral species, tends to increase from the ancient magmatic complexes to the younger ones. The line in the diagram (Fig. 3), drawn through the field of the least altered rocks, corresponds approximately to the Nb/Ta trends in time.

(e) In the instances of variations of the ratio within one and the same massif, there shows an evidence of its clear dependence on genetic characteristics of the process. The same relationships as were already noted for Zr and Hf become manifest also for Nb and Ta, although in less conspicuous forms, namely: the Nb/Ta ratios become lower in autometasomatic rocks and in pegmatites but higher in the exomorphic zones and in metasomatic veins. There is an increase in the quantities of tantalum in minerals as a function of the degree of autometasomatic reworking of the rocks (microclinization, albitization, silicification). This tendency is definitely manifest in columbites of the Erzin Massif and in fergusonites of the Agash Massif (Table 1). The good correlation of the Zr/Hf in zircons with the Nb/Ta ratio in tantaloniobates in the massifs of Dugda, Erzin, and Aksug is conspicuous. Table 3 shows the corresponding ratios for the Zr-Hf and the Nb-Ta pairs in zircons and tantaloniobates in one and the same or in nearly identical samples (the analyses of zircons are taken from an earlier publication [3] and were repeated by I. D. Shevaleevskii).

The common trend in the Nb/Ta and the Zr/Hf ratios is an indication of resemblances in the migration properties of Zr and Nb on one hand and of Ta and Hf on the other.

There are departures from these relationships in the Dugda area. The lower Nb/Ta ratios in pyrochlores from the exomorphic metasomatites (in contrast with the magmatic and the auto-metasomatic rocks of the area) is related to their very high content of minerals having volatile constituents (fluorite, apatite, carbonate). Presence of the volatile constituents appears to be conducive to greater mobility of tantalum.

(f) Studies of the Nb and Ta ratios in different minerals in cases where these minerals are present together, which is observed only in pegmatites, is a matter of some interest. Determination of the Nb and Ta content of different minerals, in relatively confined pegmatitic



Nb/Ta ratios in rocks of different age. Sample numbers are the same as in Table 1.

Table 2

Minerals	General Range of Variation of Nb/Ta	Range of Variation of Nb/Ta in Rock of Different Phase		
		Granites	Nepheline Syenites	Sub-Alkalic Rocks
Columbite	3.9 to 29	3.9 to 16	-	8 to 29
Fergusonite	3.5 to 32	3.5 to 10	-	10 to 32
Euxenite	5.7 to 100	-	-	11 to 34*
Pyrochlore	7.4 to 21	-	7.4 to 14.5	11.5 to 21
Microlite	0.5 to 2.3	0.5 to 2.3	-	-

* The ratios are up to 80-100 in euxenites from metasomatic veins, rock samples Nos. 14 and 15.

systems, may be of aid to us in the problem of the equilibria among the minor constituents.

We studied the simultaneous presence of several tantalum-niobium minerals only in the granitic pegmatites of the Khusuingol and Bayan

Table 3

No.	Sample	Zr/Hf in Zircon	Nb/Ta in Tantaloniobate	Tantaloniobate
Erzin Massif				
1	Albitized pegmatoid vein	18	8	Columbite
2	Altered alkalic granite	14	11	Columbite
3	Altered alkalic granite	17	11	Columbite
4	Altered alkalic granite	36	14.5	Columbite
6	Altered alkalic granite	39	18	Columbite
7	Altered alkalic granite	19	22	Columbite
8	Altered alkalic granite	55	29	Columbite
Aksug Massif				
10	Albitized syenite	34	14.5	Euxenite
11	Riebeckite-albite schlieren	29	22	Euxenite
13	Bostonite	38	34	Euxenite
14	Riebeckite-albite vein	66	80	Euxenite
15	Riebeckite-albite vein	145	100	Euxenite
Dugdin Massif				
36	Magnetite-quartz rock	31	10	Fergusonite
30	Riebeckite-quartz vein	30	16	Pyrochlore
32	Riebeckite-microcline vein	35	18	Pyrochlore
34	Aegirine granite	100	18	Pyrochlore
35	Aegirine albitite	91	20	Pyrochlore

The first one of these areas, columbite was formed in the early stages of the pegmatitic process, but fergusonite and microline were developed in the alkalic-enriched terminal products. Columbites and fergusonites have similar Nb/Ta ratios, on the whole; microlites are enriched with tantalum to a considerable degree.

g) The widest range of fluctuations of the Nb/Ta ratios depending on genetic environments is observed in euxenites; this may be explained presently by the low stability of the structures of this mineral.

CONCLUSIONS

The Nb/Ta ratio in minerals here investigated is related mainly to the magmatic evolution and is dependent on the relative age of the rocks, in contrast with the Zr/Hf ratio in zircons which depends on the alkalinity and genetic type of the rocks and is not related to their age. In the younger rocks there develops a certain accumulation of Nb in the younger complexes, in the course of a regional development of the magmatism.

The numerical values of the Nb/Ta ratio in minerals from different rocks of a given magmatic complex fluctuate within the same limits of variation.

The Nb/Ta ratio is not affected by alkalinity of the rocks, which is not the case with the Zr/Hf ratio. Changes in alkalinity and composition of the rocks have their expressions in the successions of tantalum minerals.

Genetic factors involved in the formation of tantalum-niobium minerals in rock complexes of one and the same age affect the magnitude of the Nb/Ta ratio in the same manner as they affect the Zr/Hf ratio, but to a lesser degree. Sudden changes in both of these ratios are characteristic only for euxenites.

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GEOCHEMISTRY OF POTASSIUM, RUBIDIUM, AND THALLIUM IN APPLICATION TO PROBLEMS IN PETROLOGY

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Abstract

Distribution of K, Rb, and Tl in igneous rocks of the Malaya Laba Massif in the Main Range of the Caucasus indicates their usefulness in interpreting geochemical processes. Age relationships in this Massif were studied predominantly by field techniques, whereby the following time sequence of intrusions was developed: 1) Tonalite (including a microclinized porphyroitic granodiorite facies); 2) Coarse grained, 2-mica microcline granite; 3) Medium- and fine-grained, 2-mica microcline, leucocratic granite and 4) Alaskite. Three samples were taken of each rock type and facies for study and analysis. K and Rb were determined by flame photometry (reliability of 15-17%). Tl by colorimetry (reliability of 15-17%). The Rb/Tl ratios for most granitoids of the Malaya Laba granitoids are similar (265-276) and indicate a common origin of the rocks in the same magma chamber. The average percentage of K in the Massif is 2.3 per cent; Rb 1.37×10^{-2} per cent; and Tl 1.37×10^{-5} per cent. K, Rb, and Tl progressively increase with increasing differentiation of the magma. However, the rate of increase of Rb and Tl is lower than the rate of increase of K; thus the K/Br and K/Tl ratios decrease in the progression tonalite-granite-alaskite. The serial progression of Rb/Tl ratios involving the coarse grained, 2-mica microcline bespeak of intrusion of this granite as a normal but independent phase in contrast to metasomatically derived porphyroid granodiorites. In the latter, the microclinizing fluids producing the feldspar porphyroblasts were evidently enriched in Tl relative to Rb as evidenced by a low Rb/Tl ratio. However, biotites of the porphyroid granodiorites show relatively high Rb/Tl ratios which may be due to the greater mobility of Tl in relation to Rb. This greater mobility of Tl may have enabled Tl to migrate out of the biotite lattice. For granitoids in general, both Rb and Tl are preferentially enriched in biotite relative to feldspar. However, the bulk of Rb and Tl is carried by feldspar since feldspar is volumetrically more abundant than biotite in the Malaya Laba Massif. Data on the distribution of K, Rb, and Tl agree with petrographical and field observations and may be used as possible tools for petrogenetic studies.

The possibility of using the geochemical characteristics of the behavior of K, Rb, and Tl in solving certain petrologic problems has been discussed repeatedly in our literature as well as abroad [2, 5, 6, 9, and others]. In the present study, based on data obtained regarding the distribution of K, Rb, and Tl, the authors endeavor to interpret their results relative to the petrology of a particular intrusive massif and to ascertain the extent of agreement between the results of petrologic and

geochemical investigations. The subject of their two-year study was the Malaya Laba massif in the Main Range of the Caucasus. Their aim was a more exact understanding of its petrologic features, in order to clarify certain problems in the geochemistry of this intrusive body.

The Malaya Laba massif has an intricate structure, developed in several successive stages in the course of the prolonged Harz tectonic magmatic cycle. The authors determined age relationships in this intrusive body by studying cross-cutting relationships of rocks of different intrusive stages by xenoliths present in different rocks, and by internal structures in different intrusive stages. Principal aspects of the results may be stated as follows in order of occurrence of rock phases:

1. Tonalites, uniformly grained, biotitic, including a microclinized porphyroblastic granodiorite facies.
2. Granites, coarse grained, microcline, 2-mica.
3. Granites, leucocratic, microcline, 2-mica, fine grained and medium grained.
4. Alaskites.

Three varieties are recognized among the tonalites of the Malaya Laba:

1. Tonalites of the northeastern margin of the massif.
2. Foliated tonalites of the Tsakhvoa River.
3. Unfoliated tonalites of the Tsakhvoa River.

The main distinction between the differentiation sequence of the Malaya Laba granitoids and the granitoids of the Main Range proposed by Afanasev [1] is our recognition of the coarse-grained microcline granites as an independent intrusive phase in the emplacement of the Malaya Laba massif. These granites would correspond to the "Rastaikinsk type" proposed by Afanasev. The results of our petrologic and petro-tectonic studies are in agreement with the current ideas regarding a metasomatic origin of the porphyroid granodiorites by a microclinization of the tonalites. However, these results cannot be construed to support the belief that the coarse-grained 2-mica microcline granites originated by the same process.

The coarse-grained granites in the vicinity of the Malaya Laba massif are an independent intrusion. This intrusion is in contact with fine-grained and medium-grained 2-mica granites in the northeast, east, and northwest of the massif and with crystalline schists in the southwest and, to some extent, in the east near the western end of the Yukha Range. We could find no direct contacts of tonalites with coarse-grained granites. However, the presence of xenoliths of tonalitic appearance and composition in the coarse-grained granites, and most important of all, the different orientation of the structural components suggest differences in the time of their intrusion. Time differences are also indicated by the more severe de-gneissification of the tonalites and by the fresher appearance of the coarse-grained microcline granites. All this evidence indicates that intrusion of the coarse-grained granites came after intrusion of the tonalites.

The alaskite phase includes primarily fine-grained and medium-grained 2-mica leucocratic granites. These granites are not particularly abundant in the massif; they resemble the alaskites closely in composition. The alaskites also form small bodies and veins associated chiefly with the leucocratic granites but crosscutting all of the Malaya Laba rocks.

On the basis of our petrologic and petro-tectonic investigations, we were therefore able to introduce certain refinements into Afanasev's differentiation scheme for granitoids of the Main Range of the Caucasus [1]. The purpose of the study was to detail geochemical characteristics with respect to K, Rb, and Tl for rocks of different age and of the Malaya Laba facies of the Malaya Laba granitoids.

For this purpose we used several samples of each variety of rock. These samples were selected to afford the most complete characterization of every member of the rock series, and with attention to the following particulars: 1. All samples were typical representatives of every member of the granitoid series. 2. All samples were fresh and without any evidence of alteration whatsoever. 3. The samples were taken from different parts of the intrusions.

As previously stated, we recognize three varieties of the Malaya Laba tonalites. For thorough representation of each rock phase, three samples were taken.

Composite samples of every rock type were prepared by mixing equal weights of the individual samples and were analyzed as a check on the analysis of their constituents. Analyzed also were average composites of mineral fractions of the same samples: feldspar and biotite—principal accumulators of K, Rb, and Tl. Quartz was also analyzed. K and Rb were determined by the flame-photometric procedure developed by Fabrikova, with a reliability of 7%. Tl was determined by the procedure suggested by Voskresenskaya [4]*, with a reliability of 15%.

DISTRIBUTION OF K, Rb, AND Tl IN GRANITOIDS OF THE MALAYA LABA MASSIF

Data on K, Rb, and Tl content in rocks of every age and variety of granitoid facies of the Malaya Laba massif obtained by the analyses are presented in Tables 1, 2, and 3. Let us consider now the behavior of these three elements separately.

Potassium. The average potassium content of the Malaya Laba massif is 2.3%. This figure does not differ very much from Vinogradov's averages [3], 2.31% for diorites and 3.34% for granites. According to our findings, potassium tends to increase from tonalites to granites. Alaskite veins contain about twice as much potassium as the tonalites.

We are indebted to A. A. Saukov, N. T. Voskresenskaya, and E. A. Fabrikova for their consultation in our work.

Table 1. Distribution of Potassium in Principal Intrusive Phases of the Malaya Laba Massif

[illegible]

Rubidium. The average rubidium content of the Malaya Laba mass is 1.37×10^{-2} . This figure, too, is close to Vinogradov's average [3]: $7 \times 10^{-3}\%$ for diorites and 4×10^{-2} for granites. The rubidium content of alaskites is more than twice that of tonalites.

Thallium. The average thallium content of the Malaya Laba mass is

Table 2. Distribution of Rubidium in Principal Intrusive Phases of the Malaya Laba Massif

[illegible]

Table 3. Distribution of Thallium in Principal Intrusive Phases of the Malaya Laba Massif

Rock	10 ⁻⁵ x % Tl in individual samples				10 ⁻⁵ x % Tl			
	1	2	3	4	Range of variation	Av.	Composite sample average	Average taken to represent entire rock
Alaskites of the eastern margin of the Malaya Laba massif	2.2	3.5	4	-	2.2 to 4	3.2	3.6	3.4
Unfoliated tonalites, Khvoa River	2.5	3	4	-	2.5 to 4	3.2	3.1	3.2
Foliated tonalites, Khvoa River	3.3	4.1	3.3	-	3.3 to 4.1	3.6	3	3.3
Average for tonalites:					2.2 to 4.1			
Coarse-grained 2-mica orthoclase granites	5.5	5	4.9	5.2	4.9 to 5.5	5.2	4.8	5.0
Microcratic granites	6.0	6.4	5.8	6.2	5.8 to 6.4	6.1	6.2	6.2
Alaskite dikes	7.1	6.8	-	-	6.8 to 7.1	7.0	-	7.0
Phenocrystic granodiorites	5.6	6.0	-	-	5.6 to 6.0	5.8	-	5.8
Average Tl in the massif: 5.5 x 10 ⁻⁵ %								

5.5 x 10⁻⁵%. This is extremely close to the thallium clark reported by Rankama [10], 0.6 x 10⁻⁴%, but is different from Shaw's results [11], 1.3 x 10⁻⁴% for igneous rocks and 3.1 x 10⁻⁴% for granites, as well as from Ahren's calculated figure [2] of 3 x 10⁻⁴%. Our figure is again within Vinogradov's range [3] from 1.5 x 10⁻⁵% for diorites to 2.5 x 10⁻⁴% for granites. It follows from these comparisons that the magmatic source to which the Malaya Laba massif owes its origin is relatively poor in thallium. In going over our data for the entire phenocrystic series of the massif, one may see that thallium is definitely accumulated in the more silicic formations. If the thallium average for the tonalites is 3.3 x 10⁻⁵%, its average for the alaskites is 7 x 10⁻⁵%.

Table 4. Summary of the Distribution of K, Rb, and Tl among the Principal Intrusive Phases of the Malaya Laba Massif

Rock	% K	% Rb	% Tl	Rb/Tl	K/Rb	K/Tl
Alaskites	1.65	0.88 x 10 ⁻²	3.3 x 10 ⁻⁵	267	187	50,000
Coarse-grained 2-mica orthoclase granites	2.48	1.38 x 10 ⁻²	5 x 10 ⁻⁵	276	180	49,600
Microcratic granites	2.82	1.64 x 10 ⁻²	6.2 x 10 ⁻⁵	265	172	45,500
Alaskite dikes	3.15	1.87 x 10 ⁻²	7.0 x 10 ⁻⁵	267	167	45,000
Phenocrystic granodiorites (bulk of the rocks)	1.3	1.08 x 10 ⁻²	5.8 x 10 ⁻⁵	186	120	22,400

THE Rb/Tl, K/Rb, AND K/Tl RATIOS

Data on the Rb/Tl ratio in granitoids of the massif are presented in Table 4. According to our findings, the average Rb/Tl ratio for the Malaya Laba granitoids is 269. Shaw gives 268 as the average ratio for granitoids.

Table 5. Distribution of Potassium in Minerals from Granitoids of the Malaya Laba Massif

Source	% Mineral in rock, average	Av. % K in mineral	K in mineral per 100 g. rock	K in mineral as % of total K in rock	% K in rock, average
Tonalites of the eastern margin:					
quartz	30	-	-	-	-
feldspar	58	2.7	1.57	96	-
biotite	12	0.49	0.06	4	-
	100	-	1.63	100	1.72
Foliated tonalites:					
quartz	21	-	-	-	-
feldspar	63	1.87	1.18	73	-
biotite	16	2.73	0.44	27	-
	100	-	1.62	100	1.62
Unfoliated tonalites:					
quartz	26	-	-	-	-
feldspar	57	1.99	1.13	72	-
biotite	17	2.44	0.45	28	-
	100	-	1.58	100	1.61
Coarse-grained 2-mica microcline granites:					
quartz	36	-	-	-	-
feldspar	60	3.67	2.2	93	-
biotite	4	4.05	0.16	7	-
	100	-	2.36	100	2.48
Leucocratic granites:					
quartz	30	-	-	-	-
feldspar	67	4.07	2.73	97	-
biotite	3	3.13	0.09	3	-
	100	-	2.82	100	2.82
Alaskite veins:					
quartz	32	-	-	-	-
feldspar	68	4.6	3.13	100	3.13
	100	-	3.13	100	3.13
Porphyroid granodiorites (bulk of the rock):					
quartz	27	-	-	-	-
feldspar	56	0.9	0.5	37	-
biotite	17	5	0.85	63	-
	100	-	1.35	100	1.30

Table 4 shows that the Rb/Tl ratio is constant for all varieties of Malaya Laba granitoids, with the exception of the porphyroid monodiorites.

The K/Rb and the K/Tl ratios are also presented in Table 4. These ratios decrease from the early to the late phases of the granitoid complex series. However, the decrease is very gradual, and, on occasion, fluctuations of the ratios are within the limits of the analytical error. One must take into account, on the other hand, that the lowering of the ratios was observed systematically in a whole series of the samples and that we are still justified in discussing the tendencies toward the lowering of the K/Rb and the K/Tl ratios in the direction indicated (*i.e.*, the tendency toward the relative enrichment of Rb and Tl versus K).

DISTRIBUTION OF K, Rb, AND Tl IN MINERALS FROM GRANITOIDS OF THE MALAYA LABA MASSIF

Our results on the distribution of K, Rb, and Tl in minerals from Malaya Laba granitoids are presented in Tables 5, 6, 7, 8, and 9. One should note that the feldspar examined was represented by different proportions of plagioclase and microcline in different granitoids of the complex. Moreover, the amounts of microcline in the complex decrease regularly from tonalites to alaskites.

Consequently, the higher content of K, Rb, and Tl shown in the tables cited here depends not only on the accumulation of these elements in the rocks formed toward the end of the magmatic process, but chiefly on the higher proportions of microcline in the feldspar fraction.

K, Rb, and Tl accumulate in microcline but are practically absent in plagioclase. Consequently, Rb/Tl, K/Rb, and K/Tl ratios in a feldspar sample derived from definite variety of the granitoids are the same as in the microcline and are independent of the microcline-plagioclase proportions. Our conclusions must be drawn therefore only from the Rb/Tl, K/Rb, and K/Tl ratios indicated here and not from the absolute quantities of these elements in the feldspars. Thus a decrease in the K/Rb and the K/Tl ratios in feldspars, notwithstanding the progressively increasing potassium content of these minerals toward the silicic end of the rock series, allows us to conclude that Rb and Tl not only are enriched during magmatic fractionation but are enriched at a greater rate than K is enriched.

In view of the foregoing considerations, comparisons between biotites and feldspars, with respect to their K, Rb, and Tl content, becomes even more difficult. However, the significantly more pronounced decrease of the K/Rb ratio in biotites (from 196 to 137 in coarse-grained tonalites and leucocratic granites respectively), versus feldspars (from 196 to 182 in coarse-grained and leucocratic granites respectively) is a clear indication that rubidium is preferentially enriched in biotites rather than in feldspars.

Table 6. Distribution of Rubidium in Granitoid Minerals of the Malaya Laba Massif

Rock	% Mineral in rock, average	% Rb in mineral ($\times 10^{-2}$)	Rb in mineral per 100 g. of rock ($\times 10^{-2}$)	Rb in mineral as % of total in rock	% Rb in rock average, ($\times 10^{-2}$)
Tonalites of the eastern margin:					
quartz	30	-	-	-	-
feldspar	58	0.86	0.5	72	-
biotite	12	1.56	0.19	28	-
	100	-	0.69	100	0.99
Foliated tonalites:					
quartz	21	-	-	-	-
feldspar	63	0.45	0.28	35	-
biotite	16	3.16	0.51	65	-
	100	-	0.79	100	0.86
Unfoliated tonalites:					
quartz	26	-	-	-	-
feldspar	57	0.72	0.41	54	-
biotite	17	2.03	0.35	46	-
	100	-	0.76	100	0.58
Coarse-grained 2-mica microcline granites:					
quartz	36	-	-	-	-
feldspar	60	1.74	1.04	56	-
biotite	4	2.07	0.83	44	-
	100	-	1.87	100	1.38
Leucocratic granites:					
quartz	30	-	-	-	-
feldspar	67	2.24	1.5	96	-
biotite	3	2.28	0.07	4	-
	100	-	1.57	100	1.64
Alaskite veins:					
quartz	32	-	-	-	-
feldspar	68	2.7	1.84	100	-
	100	-	1.84	100	1.87
Porphyroid granodiorites (bulk of the rock):					
quartz	27	-	-	-	-
feldspar*	56	0.2	0.11	10	-
biotite	17	5.51	0.94	90	-
	100	-	1.05	100	1.08

* 2.73×10^{-2} % Rb in the microcline inclusions in the porphyroid granodiorites.

The significantly more pronounced lowering of the K/Tl ratio in biotites (from 56,200 to 39,100 in coarse-grained and leucocratic granites respectively), versus feldspars (from 53,100 to 50,900 in coarse-grained and the leucocratic granites respectively) indicates the greater accumulation of thallium in biotites as compared with feldspars. However, because feldspar percentages in the rocks are much higher than

Table 7. Distribution of Thallium in Granitoid Minerals of the Malaya Laba Massif

Rock	% Mineral in rock, average	% Tl in mineral ($\times 10^{-5}$)	Tl in mineral per 100 g. of rock ($\times 10^{-3}$)	Tl in mineral as % of total Tl in rock	% Tl in rock, average ($\times 10^{-5}$)
Alkaline granites of the eastern margin:					
Quartz	30	-	-	-	-
Feldspar	58	3.8	2.2	79	-
Biotite	12	4.8	0.58	11	-
	100	-	2.78	100	3.4
Granitic tonalites:					
Quartz	21	-	-	-	-
Feldspar	63	5	3.15	80	-
Biotite	16	5	0.8	20	-
	100	-	3.95	100	3.2
Granitic tonalites:					
Quartz	26	-	-	-	-
Feldspar	57	5	2.85	70	-
Biotite	17	7.2	1.22	30	-
	100	-	4.07	100	3.3
Coarse-grained 2-mica microcline granites:					
Quartz	36	-	-	-	-
Feldspar	60	6.9	4.14	93	-
Biotite	4	7.2	0.29	7	-
	100	-	4.43	100	5
Microcratic granites:					
Quartz	30	-	-	-	-
Feldspar	67	8	5.36	96	-
Biotite	3	8	0.24	4	-
	100	-	5.60	100	6.2
Granite dikes:					
Quartz	32	-	-	-	-
Feldspar	68	10.3	7.1	100	-
	100	-	7.1	100	7.0
Porphyroid granodiorites (all of the rock):					
Quartz	27	-	-	-	-
Feldspar*	56	6.5	3.34	66	-
Biotite	17	11	1.87	34	-
	100	-	5.51	100	5.8

* $\times 10^{-5}$ % Tl in the microcline inclusions in the porphyroid granodiorites.

ite percentages, the principal carriers of rubidium and thallium feldspars and not biotites. In the literature dealing with the distribution abundance of Rb and Tl, it has been already pointed out that both these elements chiefly concentrate in biotites, because their ions are smaller than the K ion, and thus tend to replace K in structures in which the coordination number of K is higher. The coordination number of K

Table 8. Summary Table of Distribution of K, Rb, and Tl in Feldspars of the Granitoids of the Malaya Laba Massif

Rock	% K	% Rb ($\times 10^{-2}$)	% Tl ($\times 10^{-5}$)	Rb/Tl	K/Rb	K/Tl
Tonalites	2.35	0.79	4.4	180	297	53,400
Coarse-grained microcline granites	3.67	1.74	6.9	252	211	53,200
Leucocratic granites	4.07	2.24	8.0	280	182	50,900
Alaskites	4.60	2.70	10.3	262	170	44,700
Porphyroid granodiorites (bulk of the rock)	0.90	0.21	6.5	32	429	13,900
Inclusions (microcline) in porphyroid granodiorites	12.0	2.73	12.0	228	440	100,000

in biotites and feldspars is 12 and 8 respectively. Consequently, both Rb and Tl accumulate chiefly in biotite.

Our data show definitely that K, Rb, and Tl increase in biotites progressively from the early to the late phases of a granitoid rock series.

The Rb/Tl ratios are about the same in feldspars and biotites in all granitoids of the complex, disregarding the minerals from the porphyroid granodiorites and tonalites.

PROBLEMS OF FORMATION OF THE MALAYA LABA MASSIF

The Rb/Tl ratios we determined are very similar for the entire granitoid series and for their minerals, with the exception of the porphyroid granodiorites and tonalite feldspars. Ahrens [2] showed that the behavior of Rb and Tl in magmatic processes is so nearly identical that these two elements enter mineral structures almost invariably in about the same proportion. Moreover, their ratio does not depend on the mineral type but is determined entirely by their relative abundance in the primary source. Thus, rocks formed from the same magmatic

Table 9. Summary of Distribution of K, Rb, and Tl in Biotites of the Granitoids of the Malaya Laba Massif

Rock	% K	% Rb ($\times 10^{-2}$)	% Tl ($\times 10^{-5}$)	Rb/Tl	K/Rb	K/Tl
Tonalites	1.47	1.79	6.0	298	82	24,500
Coarse-grained microcline granites	4.05	2.07	7.2	288	196	56,300
Leucocratic granites	3.13	2.28	8.0	260	137	39,100
Porphyroid granodiorites (bulk of the rock)	5.0	5.51	11.0	501	91	45,500

ence must have very similar Rb/Tl ratios. In accepting this generation, we may be led to conclude that our rocks owe their origin to and the same magma chamber.

The quantities of K, Rb, and Tl in the Malaya Laba rock series increase in the progression from tonalites to coarse-grained, 2-mica microcline granites to leucocratic granites to alaskites. The geochemical tendency of K, Rb, and Tl to accumulate toward the end of the magmatic process is well known. Consequently, we may believe that the evolution of petrologic phases in the massif took place in the same sequence as granitoid rock phases in which quantities of K, Rb, and Tl progressively increase.

This conclusion is geochemical confirmation of the pattern of formation of the massif based on petrologic and petroctectonic data. It is well known that Rb^+ (1.49 Å) and Tl^+ (1.49 Å), being larger than K^+ (1.33 Å) are enriched to a greater extent than K toward the end of the magmatic process. This phenomenon finds its expression in the increasing K/Rb and K/Tl ratios. The progressively decreasing K/Rb and K/Tl ratios in the granitoids, with the concurrently increasing absolute quantities of K, Rb, and Tl, confirm once again the sequence of successive intrusions.

PORPHYROID GRANODIORITES

We did not pause to consider porphyroid granodiorites in the foregoing discussions, because the data on these rocks are not quite the same as on the other rocks of the massif.

Analyses of inclusions of microcline in the porphyroid granodiorites show relatively higher quantities of K, Rb, and Tl than are found in the other rocks and/or their constituents. This was to be expected, since microcline in porphyroid granodiorites is very high in K and must be enriched therefore in Rb and Tl which associate with K. The K/Rb and the K/Tl ratios for inclusions are higher than they are in the other rocks and in their minerals which shows that the fluids responsible for the microclinalization were significantly enriched in potassium. The Rb/Tl ratios for the microcline porphyroblasts are close to the normal Rb/Tl ratios for the Malaya Laba granitoids, which are somewhat low. This phenomenon may be explained possibly by the greater volatility of Tl compounds than Rb compounds; hence the consequent enrichment of microcline with Tl. The similarity of the Rb/Tl ratio in porphyroblasts to the normal Rb/Tl ratio for the Malaya Laba massif constitutes evidence of the association of the fluids (responsible for the metasomatism) with the same magmatic source from which the entire granitoid complex of the massif was formed.

In consideration of the K, Rb, and Tl content of the bulk of the porphyroid granodiorites (Table 4), one may see that they resemble tonalites with respect to the percentages of these three elements. This is in harmony with the opinion regarding both the porphyroid granodiorites and the microcline tonalites. Nevertheless, the Rb/Tl ratio is

too low for the porphyroid granodiorites in general (Table 4). The plausible explanation here is substantially that the thallium-enriched microclinizing fluids were instrumental not only in the formation of the microcline inclusions but were also able to affect the bulk of the rock by lowering its Rb/Tl ratio.

To support this point of view, let us turn now to the analytical data on feldspars from the main body of the porphyroid granodiorites (Table 8). This section studies show that microclinization was proceeding chiefly through cataclastic areas in the rock as well as in the feldspars. The effects of the microclinizing fluids—richer in Tl than in Pb—are reflected by the lower Rb/Tl ratios (down to 32) for the feldspars. In turn, this ratio for the entire rock is lower. The high Rb/Tl ratio in biotites from the porphyroid granodiorites may be best explained by the greater mobility of Tl, in comparison with Rb, which enabled Tl to migrate out of the biotite lattice.

The somewhat lower Rb/Tl ratios for the feldspars from tonalites (Table 8) may be similarly explained. The porphyroid granodiorites are developed in the contacts between the leucocratic granites and the alaskites. The incidence of the microcline porphyroblasts increases toward the alaskite-leucocratic granite contacts. Likewise tonalites grade gently into the porphyroid granodiorites. Microclinization is expressed, to a high degree, only near the contacts in places where the porphyroid granodiorites are well developed. However, the entire bulk of the tonalites was undoubtedly also affected by the process. As a result, the feldspars in the tonalites also show a decrease in the Rb/Tl ratio, but to a lesser degree than is shown by the feldspars in the porphyroid granodiorites. In the latter, microclinization was undoubtedly manifested to a high degree.

COARSE-GRAINED 2-MICA MICROCLINE GRANITES

The analytical data show that quantitative data on K, Rb, and Tl in coarse-grained microcline granites and in their minerals do not upset the indicated gradual increase of their content in the Malaya Laba granitoid complex series. The K/Rb and the K/Tl ratios for the coarse-grained granites and in their minerals are also in agreement with the sustained trend toward the lower ratios, from the tonalites to the alaskites. The Rb/Tl ratio for these granites and for their minerals is close to the characteristic Rb/Tl ratio for the Malaya Laba granitoids.

The facts here enumerated show that the coarse-grained microclin

*The tonalite mineral averages, cited in Tables 8 and 9, were calculated without taking into account the figures for the foliated varieties of tonalites. For sake of more complete characterization of the foliated variety, we included samples of the non-foliated areas into the composite average sample; hence the somewhat different figures (in Tables 8 and 9) compared with figures for other varieties of tonalites.

anites are the ordinary granites of the Malaya Laba massif. We have no indication of their metasomatic origin, such as the porphyroid anodiorites for example. On the contrary, geochemical evidence points to the fact that the coarse-grained granites indeed belong in the position assigned to them in our scheme of differentiation of the Malaya Laba massif. All of this constitutes evidence of the fact that the coarse-grained microcline granites were formed as an independent stage of the emplacement of the Malaya Laba massif.

CONCLUSIONS

1. Data on the distribution of K, Rb, Tl agree with the results of petrographic investigations, and may be useful, on occasion, as indicators of possible avenues of study conducive to solutions of some still obscure petrologic problems.
2. The Rb/Tl ratios for all varieties of the Malaya Laba granitoids as a whole, as well as for the granitoid minerals, are very similar and are indicative of a common origin of the granitoids in one and the same magma chamber.
3. The progressively increasing content of K, Rb, and Tl in the granitoid series, from tonalites to coarse-grained 2-mica microcline granites to leucocratic granites to alaskites, and the tendency toward increasing K/Rb and K/Tl ratios in the same direction confirm the indicated successions of rock phases in the formation of the Malaya Laba intrusive body. This fact is in agreement with the pattern of emplacement of intrusions for the Malaya Laba massif, based on petrologic observations.
4. The Rb/Tl ratios for the coarse-grained 2-mica microcline granites and for their minerals characteristic of the Malaya Laba massif and the absence of any anomalous features of the K, Rb, and Tl distribution in these rocks, indicate that the intrusion of the granites is an independent phase (in the formation of the massif). This relationship also indicates that all of the rocks of the massif originated in one and the same magmatic source.
5. The analytical data on the porphyroid granodiorites are in accord with the theory of their metasomatic origin. The Rb/Tl ratios for the porphyroblasts are close to those in the Malaya Laba granitoids, in general. This leads us to the supposition that the fluids responsible for the metasomatization originated in the same magmatic source as the entire granitoid complex of the Malaya Laba. Because of their relatively higher volatility, Tl compounds were enriched in the fluids to a higher degree than Rb compounds.
6. A consideration of the Rb and Tl distribution in the granitoid minerals indicates their preferential accumulation in biotites relative to feldspars.
7. The enrichment of Rb and Tl in feldspars of the relatively more acidic rocks is more intensive than the enrichment of K.

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THE DISTRIBUTION OF SCANDIUM AND NIOBIUM IN WOLFRAMITES

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Abstract

The examination of 350 wolframite samples from 42 deposits has shown:
1) Niobium does not constantly accompany scandium in wolframites. V. Goldschmidt's hypothesis, according to which a heterovalent replacement FeWO_4 in wolframites by ScNbO_4 takes place, obviously is not universal. As a rule scandium accumulates in wolframites of rare-metal deposits of greisen type, whereas niobium may enter the composition of wolframites in a wider temperature interval. Wolframites from deposits of the greisen type, like those of typical hydrothermal deposits, contain scandium.

In 1931, V. M. Goldschmidt and C. Peters [1] suggested that scandium is present in wolframite because of its heterovalent replacement of divalent iron and manganese. The valences are balanced by replacement of a trivalent negative group, NbO_4^{3-} or TaO_4^{3-} , by a divalent negative group, WO_4^{2-} . V. M. Goldschmidt studied specimens of scandium-rich wolframite (up to 1% Sc_2O_3 *) and showed that they contain about 1% Nb_2O_5 and 0.5% Ta_2O_5 . The amounts of tantalum and niobium he found are sufficient for the isomorphism of ScNbO_4 , ScTaO_4 with FeWO_4 and MnWO_4 . This hypothesis of Goldschmidt, based on the concepts of magnitudes of the charges and sizes of the ions, was accepted by many other investigators.

In 1951, F. Leutwein [2], in his studies of the Zinnwald Erzgebirge wolframite and of some from some other sources, concluded that replacements of this sort are impossible in wolframite structures, for several reasons: a) A simultaneous content of equivalent quantities of scandium oxide and of niobic acid fails to produce any scandium niobate; b) the crystal-lattice energy of scandium niobate is about three times as high as those of iron or manganese niobates and about four times as high as those of iron or manganese tungstates.
F. Leutwein explains the presence of scandium in wolframite by a substitution of the trivalent scandium ion, Sc^{3+} , for the divalent iron ion, Fe^{2+} , without balancing of the charges. He believes that a substitution of this kind is possible because of the small amounts of scandium present in the wolframite (not over 0.2 to 0.3%). As to the presence of niobium and tantalum in wolframites, this is explainable by anomalous mixed crystals and not by isomorphism.

* L. Goldschmidt's data.

Our studies support the conclusions of F. Leutwein, to a certain degree. Specifically, an appreciable proportion of our samples of wolframite in which scandium is present contains no detectable niobium.

As the result of our analysis of 350 samples of wolframite from 48 deposits, we are able to show that niobium generally, but not invariably is found together with scandium (Table 1). 59 out of 234 samples of wolframite, i.e., about 25%, containing scandium do not contain any niobium. On the other hand, a large number of samples, 69, contain appreciable amounts of niobium (up to 0.3% Nb_2O_5) but no scandium.

Table 1. Distribution of Scandium and Niobium in Wolframites from Rare Metal Deposits of the USSR

Sc	Nb	Number of Samples	Number of Deposits
+	+	175	22
+	-	59	11
-	+	69	20
-	-	54	14

+ = present; - = absent

The results here cited show that scandium is not invariably a niobate, in wolframites, since niobium may be absent. Tantalum could not be detected in most of the samples analyzed by us, with the exception of the wolframites from Dedova Gora, Polyarnoe, and Spokoinoe. On the other hand, niobium in wolframites is not invariably a scandium niobate. As already stated, more than 25% of the niobium-bearing wolframites contain no scandium. Thus the available statistical data indicate possibilities of some other forms for entry of scandium and niobium into wolframite structures, which are not the same as the mechanisms visualized by V. M. Goldschmidt.

The diagram here shown (Fig. 1) illustrates the occurrence of Sc_2O_3 and Nb_2O_5 in wolframites, for a group of rare-metal deposits of the pneumatolytic-hydrothermal type. The diagram shows no direct correlation between the amounts of scandium and niobium in wolframites. Moreover, one may see from the results reported in Table 2, in the instance of some ore bodies of the scandium-bearing Akchatau Deposit, the scandium content of wolframites is not necessarily contingent on the presence of niobium. Titanium, common in wolframites, may function as an anion, in such cases, so as to compensate for the difference in the ionic charges. F. Leutwein may be right, possibly, in suggesting that scandium, Sc^{3+} , may replace divalent iron, Fe^{2+} , without any compensation of the ionic charges.

Comparisons of the analyses of wolframites from different rare-

al deposits of the USSR, by Institute of Mineralogy, chemistry, and Crystal mistry, Academy of nces of the USSR, allowed o prove certain relation- s in the distribution-abun- e of scandium and niobium ole 3). Namely, both scan- n and niobium are present olframites of the majority gh-temperature pneumato- e-hydrothermal deposits of greisen and quartz-greisen s (Table 3, Column 1), such olyarnoe, Akchatau, Bain- , Sherlova Gora, and rs.

here are some departures n this relationship in the atau, where some of the dium-bearing wolframites contain no niobium. It should be noted such scandium-bearing niobium-free wolframites are found only me clearly defined ore bodies in the southeastern part of the sit.

olframites from some medium-temperature hydrothermal deposits utinskoe, va Gora) con- only niobium le 3, Column

he absence of scandium and um was ed only in wol- ites from um-tempera- hydrothermal sits (Aldaka- Bukuka, and others)

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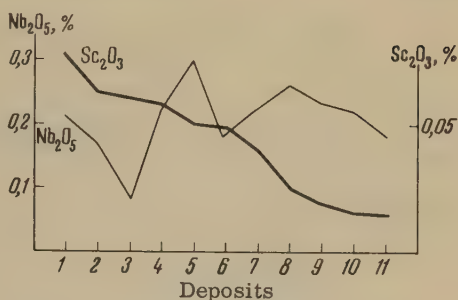


Fig. 1. Character of the distribution of Sc_2O_3 and Nb_2O_5 in wolframites of pneumatolytic-hydrothermal deposits of USSR. Deposits: 1—Polyarnoe; 2—Akchatau; 3—Kamenka; 4—Bainazar; 5—Etyka; 6—Sherlova Gora; 7—Darat; 8—North Kounrad; 9—Kara-Oba; 10—Vol'framitovye (Sopki); 11—East Kounrad (in order of decreasing average content of Sc_2O_3).

Table 2. Contents of Sc_2O_3 and Nb_2O_5 of Wolframites in Certain Mineralized Veins of the Akchatau Deposit*

Sample No.	Vein No.	% Sc_2O_3	% Nb_2O_5
1032	2	0.05	Not detected
1083	2	0.05	Not detected
1085	2	0.05	Not detected
1086	2	0.07	Not detected
1088	2	0.05	Not detected
1130	2	0.07	Not detected
1035	3	0.05	Not detected
1090	3	0.05	Not detected
1092	3	0.02	Not detected
1094	3	0.05	0.074
1099	3	0.05	Not detected
1179	3	0.05	Not detected
1181	3	0.07	Not detected
1118	6	0.07	Not detected
1119	6	0.055	Not detected
1122	6	0.07	Not detected
1124	6	0.057	0.07

*Sensitivity of the method: 0.005%

Table 3. Average Content of Sc_2O_3 and Nb_2O_5 in Wolframites from Various Rare Metal Deposits

Type	1				2		
	Deposit	No. of Analyses	% %, Average		Deposit	No. of Analyses	% Sc_2O_3 Average
"A" Pneumatolytic- Hydrothermal	Zinnwald, Erzgebirge*	11	0.26	0.45	Zhannet, Central Kazakhstan	3	0.06
	Polyarnoe, NE Asia	22	0.076	0.21	Akchatau, Central Kazakhstan	26	0.05
	Akchatau, Central Kazakhstan	54	0.062	0.17	Kara-Oba, Central Kazakhstan	1	0.02
	Kamenka, Altai	3	0.06	0.08			
	Bainazar, Central Kazakhstan	10	0.059	0.23			
	Etyka, E. Transbaikal	2	0.05	0.30			
	Sherlova Gora, E. Transbaikal	15	0.049	0.19			
	Darat, Central Kazakhstan	4	0.04	0.22			
	North Kounrad, Central Kazakhstan	9	0.024	0.26			
	Kara-Oba, Central Kazakhstan	35	0.02	0.23			
	Volframovye Sopki, Central Kazakhstan	4	0.016	0.22			
	East Kounrad, Central Kazakhstan	8	0.015	0.18			
"B" Hydrothermal	Antonova Gora, E. Transbaikal	3	0.005	0.12	Belukha, E. Transbaikal	2	0.00
					Bukuka, E. Transbaikal	9	0.00

*F. Leutwein's data: 1. Both scandium and niobium present; 2. scandium present; niobium not detected; 3. scandium not detected; niobium present; 4. scandium and niobium not detected.

high-temperature rare-metal deposits of the greisen type classified us under the "A" group (Zinnwald, Polyarnoe, Bainazar, Sherlova Gora). Wolframites from the North Kounrad and from the Volframovye Sopki are also included in this group, although their scandium-niobium relationship is not as definite as in the former ones; such wolframites are found in Columns 1, 2, and 3 of the table. Characteristically, greisenization in these latter deposits is significantly weaker than in the Polyarnoe or the Sherlova Gora, etc., whereas, genetically they are closer to deposits of the medium-temperature hydrothermal type. On the other hand, wolframites from deposits in the "B" group but showing certain signs of greisenization, are found in Columns 2, 4, and even 1 of the table (Bukuka, Belukha).

In such a manner, if we compare the distribution-abundance of the two elements in wolframites from genetically different deposits, it will develop that scandium constitutes a characteristic admixture in wolframites from the high-temperature pneumatolytic-hydrothermal ve-

Table 3. (Continued)

Type	3			4	
	Deposit	No. of Analyses	% Nb ₂ O ₅ Average	Deposit	No. of Analyses
"A" Pneumatolytic-Hydrothermal	Kara-Oba, Central Kazakhstan	3	0.30		
	North Kounrad, Central Kazakhstan	3	0.12		
	Volframovye Sopke Central Kazakhstan	5	0.18		
"B" Hydrothermal	Belukha, E. Transbaikal	2	0.07	Belukha, E. Transbaikal	13
	Bukuka, E. Transbaikal	2	0.16	Bukuka, E. Transbaikal	23
	Spokoinoe, E. Transbaikal	8	0.43	Spokoinoe, E. Transbaikal	3
	Kalgutinskoe, Altai	4	0.15	Kalgutinskoe, Altai	1
	Dedova Gora, E. Transbaikal	9	0.014	Aldakachan, E. Transbaikal	6
	Antonova Gora, E. Transbaikal	20	0.08		

whereas niobium is able to enter wolframites within a wider range of temperature variation. Niobium is very common in wolframites both of the pneumatolytic-hydrothermal and of the typically hydrothermal type (to a somewhat greater extent in the former ones).

CONCLUSIONS

V. M. Goldschmidt's hypothesis of a heterovalent replacement of Nb₂O₅ by ScNbO₄ in wolframites appears to be not as generally valid as has been believed up to the present. This conclusion results from numerous examples of niobium absence in wolframite specimens in which niobium is present.

Scandium, as a rule, accumulates in wolframites of the highest-temperature rare metal deposits of the greisen type, whereas niobium enters the wolframite structures within a wider range of tempera-

ture. Wolframites in deposits of the greisen type, as well as in many others, typically hydrothermal ones, may also contain niobium.

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THE GEOCHEMISTRY OF PHOSPHORUS IN THE
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Abstract

The investigation shows that phosphorus distribution in the iron-ore formation is of a random character but follows definite regularities, related chiefly to processes of sedimentation and supergenesis. The iron-ore formation being in general very poor in phosphorus, relative accumulations of the latter occur in iron ores which originally were sediments of the leptochlorite facies. The amount of phosphorus in ores increases with depth in those cases where they lie in unmetamorphosed host rocks. In the course of supergene oxidation and leaching, removal of phosphorus reaches half and more of its original content. These regularities provide additional data for a general geochemical characterization of sedimentation and subsequent alterations of the iron-ore formation and may also be useful for stratigraphic correlation of its various lithological horizons.

Ferruginous rocks of the Krivoi Rog yield high-grade concentrates of phosphorus, which are being upgraded and are now being exploited on a commercial scale. An understanding of the relationships governing the distribution and abundance of phosphorus in these rocks is a matter of both practical and fundamental interest, because phosphorus is one of the principal deleterious impurities in the iron.

The average content of phosphorus in the earth's crust has been determined with good accuracy. A. E. Fersman accepted F. Clarke's value of 0.12%. More recently, A. P. Vinogradov [1, 2] reported 0.1% as the most likely value. There is no accumulation of phosphorus in the most common kinds of sedimentary rocks, such as sandstones, quartzites, limestones, clays, etc., and the average content of phosphorus in these sediments is lower than in the earth's crust. Siliceous and carbonate rocks are especially deficient in phosphorus. Not considering phosphates and glauconites, as they are outside the scope of the present communication, any noticeable accumulation of phosphorus occurs only in certain marsh and lacustrine sediments and, very rarely, in chiefly ferruginous marine sediments. It should be pointed out that even fairly large accumulations of phosphorus compounds, particularly calcium phosphate, are not merely common in ferruginous sediments and in sedimentary iron ores of the post-Cambrian erozoic epochs, but are practically a rule, as has been reported in the literature on many occasions. Moreover, the silicate facies are

richest in phosphorus, the carbonate facies are poorest and the oxide facies are intermediate [3].

According to modern views [4], phosphorus is precipitated from supersaturated solutions by chemical mechanisms chiefly in the central and upper parts of the continental shelf, at depths of 50 to 100 meters at low temperatures, and in oxidizing environments. Phosphorus yields gaseous compounds in oxygen-free reducing environments containing hydrogen sulfide; hence the deficiency of phosphorus in such facies [4, 5, 6].

Phosphorus may also be precipitated from unsaturated solutions in certain environments along with sedimentary iron ores of different types: those oxides and silicates that form in the presence of oxygen. Such associations of phosphorus with sedimentary iron ores may be explained by the formation of complex anions of the $\text{PO}_4^{-3} \cdot \text{FeO}_4^{-5}$ type that are hydrolytically decomposed in alkaline media with the formation of iron hydroxides and basic iron phosphates [7]. The quantitatively preponderant iron hydroxides in aqueous media easily capture the phosphates during their coagulation.

As a rule, there is little phosphorus in Precambrian ferruginous rocks of the Krivoi Rog type. The facies relationships in the distribution of this element, as here indicated, are not easily determinable, possibly because the original character of the facies is not always clear in the most ancient and highly metamorphosed ferruginous sediments. In any case, the phosphorus content of Precambrian jaspilites and ferruginous hornfelses of the USSR, USA, Brazil, South Africa, and other countries is much lower than of the iron ores belonging to later geologic epochs and is below the average of the earth's crust in the majority of cases [1, 3, 5, 8-15, and others].

Passing directly to the distribution-abundance of phosphorus in the Krivoi Rog ferruginous rocks, we must point out first of all that all of their phosphorus is contained in very small grains of apatite and has a layer-by-layer distribution. The more or less rounded grains of apatite are generally only thousandths of one millimeter in diameter; the coarser grains of apatite, as well as the locally crystalline apatite, are formed only in the more thoroughly metamorphosed rocks, which show that apatite was crystallized together with the other constituents of these rocks through successive stages of the metamorphism.

We should note that the same type of laminar distribution of apatite, an indication of its primary-sedimentary origin, was also observed in the other Precambrian ferruginous formations by other investigators [15 and others]. In this connection, divergent ideas of Tanatar should not be overlooked. He regards the apatite as a metasomatic formation of epigenetic origin caused by the action of phosphorus anhydride on the calcium hornfels (which, incidentally, is absent in most of the ferruginous rocks). These ideas must be rejected inasmuch as they are not supported by any actual data.

As we know, the Saksagan Series of crystalline schists consists of three divisions. The upper one, K_{III} , includes the mica and "carbon

ts with pockets of carbonate rocks; the lower one, K_I , includes lites and arkosic sandstones; the middle one, K_{II} , the iron-ore nation, consists of interbedded horizons of quartz-iron rocks (ferrous hornfels and jaspilites), and slate schists which always contain interlayers of hornfels.

he primary-sedimentary metamorphosed ores [17] as well as the "ferruginous" schists, the characteristic hydrogeothite-clay-quartz schists which are the products of a deep weathering chiefly of the ferropelite (leptochloritic) horizons, are present at the contact between the upper division of the Saksagan Series and the ferruginous formations.

Table 1 presents the data on phosphorus in all of the horizons here investigated, although the figures for different horizons are by no means of the same accuracy. Specifically, the figures for the ferruginous horizons are based on the vast number of data accumulated over many years of mining as well as by the special NIGRI* studies, while in the case of the other horizons we have only a relatively small number of analyses indicative merely of orders of magnitude. Numerous

Table 1. Phosphorus Content of Different Stratigraphic Horizons of the Saksagan Series

Rock	Stratigraphic Index	% Phosphorus	
		Range of Variation	Average
Carbonates	K_{III}	0.009 to 0.174	0.040
Quartz-mica schists	K_{III}	0.010 to 0.100	0.030
"Carbon" schists	K_{III}	0.020 to 0.150	0.060
"Ferruginous" schists	K_{III}	0.022 to 0.460	0.160
Primary-sedimentary ores, metamorphosed	K_{II-III}	0.012 to 0.306	0.113
Hornfels and jaspilites	K_{II}^{1-2}	0.032 to 0.132	0.065
Hornfels and jaspilites	K_{II}^4	0.024 to 0.098	0.047
Hornfels and jaspilites	K_{II}^{5-7}	0.013 to 0.082	0.037
"Carbon" schists	K_{II}	0.013 to 0.038	0.020
White, amphibolite, and pigmented schists	K_{II}	0.007 to 0.296	0.080
Schists	K_{I-II}	0.016 to 0.037	0.026
Lites	K_I	0.010 to 0.013	0.012
Sedimentary sediments	K_I	0.012 to 0.020	0.016
Average			0.036

geologic data on individual mines, reconnaissance and exploration studies for different areas of the ferruginous rocks, and published results went into the compilation of Table 1. The figures for the ferruginous rocks are weighted means (on an areal basis); the others are arithmetical averages of the available analyses.

Certain definite conclusions can be drawn from a consideration of Table 1. The Saksagan Series as a whole is very low in phosphorus with an average value of 0.036% which is approximately one third of the average for the earth's crust. The same also applies to individual horizons of the schist series. The only exceptions are the pockets of the ferrosilicate schists (amphibole, chlorite, and their analogues in the weathered crust: the "pigmented" and the "ochreous" schists) and the metamorphosed primary-sedimentary ores where levels of phosphorus rise to its average content in the earth's crust, and even exceed this average several-fold in a number of instances. There is a consistent decrease of phosphorus content with depth of the stratigraphic section within the ferruginous formation itself, according to horizons. This trend is in harmony with the sequence of the facies: the fairly extensive iron-silicate residue of the leptochlorite facies in the lowest horizons, whereas the upper horizons are composed almost entirely of residues of the oxidized facies represented, at this time, by silica-feld jaspilites and hornfelses.

The figures here cited refer to entire stratigraphic horizons. Practically all the ferruginous rocks of the Krivoi Rog, however, are characterized by alternating thin layers of ore and gangue materials (preponderantly quartzitic). For this reason, variations in the phosphorus content from one of the thin layers to another are a subject of considerable interest in conjunction with the general relationships already discussed. With this purpose in mind, we selected samples from the "ore" and the "gangue" layers and analyzed them for iron and phosphorus. The generalized results are presented in Table 2.

The first and the most important relationship indicated by the layer-by-layer analyses is the much higher content of phosphorus in the "ore" than in the "gangue" layers (quartzitic): the ore layers contain nearly three times as much phosphorus as the hornfels layers (0.065% as against 0.022%). The ore-hornfels ratio of phosphate ranges from 1.8 to 5.2, and the most striking difference in the phosphorus content is observed in the most coarsely layered rocks in which the ore and the hornfels layers are especially clearly defined.

At the same time, there is no direct proportionality between phosphorus and iron contents of the rocks, although accumulations of phosphorus are found mainly in the ore horizons (containing up to 70% of the total phosphorus of the formation). These relationships become even more conspicuous if the analyses of the ore and of the quartz layers are segregated into groups, depending on their iron content, and if the P/Fe ratios are calculated separately for every group. It becomes clear then that as the concentration of iron is quadrupled the concentration of phosphorus divided by the concentration of iron

reases by a factor of 1.5 to 2; with Fe up to 20% the ratio is 0.0018 to 0.0022, with Fe at 40 to 60% and higher the ratio is only 0.0013 to 0.0014.*

It is clear, therefore, that not all the phosphorus is associated with iron. A certain small fraction of the phosphorus is captured by silica during sedimentation, either by adsorption at the surface of the siliceous precipitate or by occlusion, i.e., by incorporation of phosphate ions into the siliceous precipitate at the time of its formation [18, 19, and others].

As to reasons for the layer-by-layer variation of the phosphorus content and to the tendency toward higher amounts in the ore layers, we may call attention to the possible importance of seasonal fluctuations in alkalinity of the solutions in which iron and silica migrate, in addition to the foregoing considerations. Thus, in the opinion of several investigators [20 and others], in tropical climates iron is leached out in acid solutions during the humid and hot seasons and is precipitated in alkaline environments, while silica is leached out by ordinary weakly alkaline waters during the cooler and not so humid seasons and is precipitated in acid environments developed by accessions of large quantities of acid (humus) solutions during the preceding season. The chemical properties of P_2O_5 (the marked increases in its solubility at very low as well as at very high pH levels and its practical insolubility in neutral or alkaline media) should be also conducive, under such conditions, to the preferential migration of phosphorus along with iron rather than with silica.

The general lithologic-geochemical and facies environments where accumulation of phosphorus takes place, in conjunction with the precipitation of iron and silica in the horizons of the ferruginous suite, will not be discussed in their entirety in this article. Even a brief review of the literature dealing with the controversial problems involved in the sedimentation and diagenesis of iron and silica in the Krivoi Rog type of formation would exceed the bounds of any ordinary journal article and, for that reason, we must confine ourselves to only a few remarks.

We should note, first of all, that the general impoverishment of the iron-ore formations of the Krivoi Rog type with respect to phosphorus as reported originally by Strakhov [11], may be accounted for by differences between the modern and the ancient oceanic waters and the atmospheres (the high CO_2 in the ancient atmosphere and, consequently, the high partial pressures of this gas); several of our own and foreign investigators agree with this view [Strakhov, 11; MacGregor, 21, and others]. Both of these factors** could have impeded the deposition of phosphorus in any appreciable quantities.

There is an apparent disharmony here between the figures in the text and in Table 1, which shows that, with Fe at 47 to 61%, the P/Fe is 0.0003 to 0.0029; with Fe at 7 to 34%, the P/Fe is 0.0007 to 0.0027. VPS
the very low P background in the progenitors of the Fe-SiO₂ rocks and the low CO_2 content of the ancient atmosphere. VPS

Table 2. Summary of Iron and Phosphorus Content of Ore and No-Ore Horizons

Rock	Stratigraphic Horizon	Number of Determinations	Ore Horizons			
			% Fe	% P	P/Fe $\times 10^4$	Concentration Coefficient
Magnetite hornfels, with silicates and carbonates	I _{Zh}	1	56.0	0.115	20	1.0
Magnetite hornfels, with silicates and carbonates	II _{Zh}	1	59.4	0.053	9	0.4
Martite hornfels	II _{Zh}	3	55.8	0.087	16	0.7
Magnetite-Chlorite hornfels	IV _{Zh}	8	47.6	0.093	20	0.8
"Pigmented" martite hornfels	IV _{Zh}	1	46.9	0.049	10	0.4
Martite hornfels	V _{Zh}	2	52.1	0.015	3	0.1
Jaspilites	V _{Zh}	1	57.5	0.037	7	0.3
Martite hornfels	VI _{Zh}	3	50.9	0.065	13	0.5
"Pigmented" martite hornfels	VII _{Zh}	1	47.4	0.065	12	0.5
Primary-sedimentary metamorphosed ore, with hornfels interlayers	K _{III} ¹	1	61.0	0.176	29	1.5
Average, for the first nine rocks	-	21	52.7	0.065	12	0.5

As we know, in the ferruginous formation of the Krivoi Rog Basin there is an interbedding of sediments belonging to different geochemical facies [22, and the earlier articles by the author]. Specifically, the silica-free rocks, especially the hematite-hornfels and the jaspilites, must be regarded as the oxidized facies of the entirely chemogenic sediments. On the other hand, the iron-silica schists belong to the typical leptochloritic facies containing substantial quantities of pelitic materials in its final residue. Such facies are characterized by an absence of excesses of both oxygen and of organic substance and by oxidation-reduction potentials only slightly below their levels in freshly formed sediments. As we know, however, these particular facies in the sediments of the younger geologic epochs produce very large accumulations of phosphorus in their ferruginous layers, including even the definitely iron-phosphate ores [11].

It becomes entirely clear, therefore, as to why there is an increase in phosphorus from the magnetite-hematite jaspilites through magnetite-silicate hornfels to iron-silica schists. The small but nevertheless noticeable accumulations of phosphorus, in contrast to its generally low background, that is observed in the chlorite, the "pigmented" and the "ochreous" schists, and in the primary-sedimentary metamorphosed ores of the Krivoi Rog iron ore formation, are evidently the first weak expressions of the process which resulted, in later geologic epochs, in immense accumulations of phosphates in the silicate iron ore horizons we have already discussed.

Limiting our discussion by the foregoing remarks, let us now consider the secondary migrations of phosphorus. Variations in the

Table 2. (Continued)

Rock	No-ore Horizons				$\frac{P \text{ "ore horizons"}}{P \text{ "no-ore horizons"}}$
	% Fe	% P	P/Fe $\times 10^4$	Concentration Coefficient	
Magnetite hornfels, with silicates and carbonates	11.0	0.022	20	0.2	5.2
Magnetite hornfels, with silicates and carbonates	12.4	0.030	25	0.3	1.8
Martite hornfels	10.6	0.020	27	0.2	4.3
Magnetite-chlorite hornfels	24.4	0.057	25	0.5	1.9
"Pigmented" martite hornfels	31.5	0.021	7	0.2	2.3
Martite hornfels	7.3	0.007	10	0.06	2.1
Jaspilites	11.1	0.008	7	0.07	4.6
Martite hornfels	17.9	0.017	10	0.4	3.9
"Pigmented" martite hornfels	16.4	0.019	12	0.2	3.4
Primary-sedimentary metamorphosed ore, with hornfels interlayers	33.5	0.046	14	0.4	3.9
Average, for the first nine rocks	15.9	0.022	16	0.2	3.0

ntity of this element, obviously related to the late stages of the geologic history of the iron ore complex, are observed locally, in addition to the layer-by-layer and the horizon-by-horizon variations that were determined essentially by the sedimentational environments and by diagenesis. In order to ascertain the causes of these secondary variations, we studied the fluctuations in the content of phosphorus in relation to the degree of oxidation of the ferruginous rocks, presence or absence of rich epigenetic ores and, finally, the depth of the deposition. The results of our studies reveal a very interesting situation. The relationship between the phosphorus content and the mineralogic composition of the rock is made conspicuously clear by data presented in Table 3. Highest phosphorus is found in the magnetite rocks, and the least in the martites and the iron-mica-martite hornfels and jaspilites. Magnetite-martites contain somewhat less phosphorus than the magnetites in the samples used by us for the calculations. However, very changes in the mineralogic composition of the rocks, from magnetite to martite, are essentially secondary and are related to intensive processes of the supergene oxidation [22, 23, 24, 25, and others]. Indeed, the distribution of phosphorus in the unoxidized and oxidized varieties of ferruginous rocks in clearly defined stratigraphic horizons (Table 4) confirms the fact that the phosphorus content falls off from the unoxidized to the oxidized zone. Such decrease in phosphorus is insignificant in some cases, but in other cases one-third of the total original phosphorus or even more is lost during oxidation.

Because oxidation of ferruginous rocks is essentially a supergene

Table 3. Range of Variations and Average Content of Phosphorus in Representative Technologic Samples of Ferruginous Rocks (as mineralogic varieties)

Varieties of Ferruginous Rock	Number of Samples	% Phosphorus	
		Range of Variations	Average
Magnetite, silicate-magnetite, and silicate-carbonate-magnetite hornfels	15	0.025 to 0.110	0.048
Magnetite-martite hornfels	5	0.018 to 0.050	0.034
Pigmented-martite hornfels	4	0.021 to 0.034	0.026
Martite hornfels	3	0.016 to 0.028	0.022
Martite and iron-mica-martite jaspilites	6	0.010 to 0.028	0.017

process despite its high intensity and its local penetration to great depths, it tends generally to weaken with depth. We attempted, therefore, to investigate the behavior of phosphorus in parts of the Saksagan Bed II that are characterized by complete oxidation of the rocks down to 1000 meters or deeper. As shown in Table 5, there is a definitely noticeable increase in phosphorus with depth (by 0.07 to 0.015%) in two out of three areas examined.

Finally, proceeding from the same empirically ascertained fact that the rich ore zones within the Saksagan Belt (regardless of the hypothetical origin of the rich ores) coincide with the areas of a complete oxidation, we undertook studies of the range of variation and of the average phosphorus content of ferruginous rocks inside and outside the zones of the high-grade ores. The appropriate calculations for the entire Saksagan Belt, presented in Table 6, illustrate clearly the decrease of phosphorus within the confines of the high-grade ore zones that also exhibit maximum oxidation.

Table 4. Changes in Content of Phosphorus in Relation to Oxidation of Ferruginous Rocks

Area	Stratigraphic Horizon	% Phosphorus		
		Unoxidized	Oxidized	Difference $\pm$
Pervomaiskii No. 2	V-VI	0.053	0.046	-0.007
Pervomaiskii No. 2	V-VI	0.114	0.069	-0.045
Frunzenskii No. 6	VI	0.024	0.019	-0.005
Bolshaya Gleevatke	I	0.079	0.046	-0.033
Bolshaya Gleevatke	II	0.064	0.018	-0.046
Bolshaya Gleevatke	IV	0.023	0.033	+0.010
Inguletskii No. 12	I	0.080	0.076	-0.004

Table 5. Changes in Phosphorus Content of Ferruginous Rocks with Depth

Area	Iron-ore horizon	% Phosphorus		
		Mine workings at 200 to 300 m.	Boreholes, 300 to 800 m.	Difference, $\pm$
Chonikidze Mine	VI	0.030	0.028	-0.002
Chonikidze Mine	VII	0.029	0.028	-0.001
Party Congress Mine	V	0.018	0.033	+0.015
Party Congress Mine	VI	0.019	0.028	+0.009
Giebknecht Mine	V	0.032	0.033	+0.001
Giebknecht Mine	VI	0.019	0.026	+0.007

It should be noted here that nearly all who had studied the Krivoi district, whether they belonged to the hypogene or the supergene schools, had emphasized the alkaline character of their hypothetical leaching or oxidizing solutions. However, solution of apatite and leaching of phosphate require acidic media. It appears reasonable, therefore, to visualize a two-stage supergenesis, with an alkaline first stage and an acidic second stage.

This article is a report of earlier results of studies that are now being continued by the author.

CONCLUSIONS

As shown by the studies here reported, the distribution of phosphorus in the ferruginous formation is not random but is determined by definite relationships that are related primarily to sedimentation and supergenesis.

In contrast to the general impoverishment of the ferruginous formation with respect to phosphorus, there is a relative enrichment of phosphorus in the ferruginous layers of the rock in keeping with the chemical character of this element. The greatest accumulations of phosphorus are found in the ferruginous horizons that were originally the residues of the leptochlorite facies.

Table 6. Variations in Phosphorus Content of Ferruginous Rocks of the Saksagan Bed II in Different Areas (inside and outside the mineralized zones)

Area	% Phosphorus	
	Range of Variation	Average
Mine shafts (containing beds of rich ore)	0.021 to 0.038	0.03
Intervals between Mine Shafts (no rich ore)	0.023 to 0.082	0.05
Entire Saksagan Bed II	-	0.04

Up to one half, and more, of the original phosphorus content of the rocks may be lost during the supergene processes. Such losses of phosphorus are characteristic particularly of the high-grade ore deposits of the Saksagan type.

The relationships here observed constitute supplementary data in aiding the general geochemical characterization of the sedimentation and of the subsequent alterations of ferruginous rocks. These same relationships may be employed in stratigraphic correlations of different lithologic horizons of the ferruginous formation.

Having ascertained that the causes of the differences in the phosphorus content of ores are rocks in the Saksagan Belt, we are able to make a prognosis to the effect that the phosphorus content of these ores will increase with depth up to its average content in the unoxidized stratigraphic horizons that are the hosts of the iron ore. The relationships established in this study shall be of definite use in the problems involved in the production of low-phosphorus concentrates of the iron ores.

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THE DISTRIBUTION OF ORGANIC MATERIAL IN BAT-BAYOS SEDIMENTS OF DAGESTAN

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Abstract

Study of the organic material of the sediments of Bat-Bayos, Dagestan, has shown that on the whole they are characterized by a lowered content of organic carbon (0.643%). The enrichment of rocks in organic matter depends on the lithological peculiarities of the rocks, the degree to which they are weathered and the proximity of the score line. The organic matter of the studied rocks is chiefly an insoluble organic component. The lesser part is bitumen. Humic acids are absent. The share of bitumen in the organic matter of rocks increases from clays to aleurolites and sandstones. That indicates that it has been formed in the latter by migration from clays.

Middle Jurassic sediments in the Caucasus, and especially the Bat-Bayos sediments, are regarded by many investigators as potential petroleum source beds from which the Mesozoic oil and gas fields have been derived [1, 2, 3, 4, 5, 6]. This view is based on general geological considerations, the appearance of oil and gas, and the disseminated bituminous substance in the sediments. The organic material of these sediments has been insufficiently studied, although a quantitatively studied distribution of organic material together with its qualitative characteristics, and the geologic and geochemical factors, are among the principal criteria in the differentiation of petroliferous suites. With this idea in mind, we undertook certain studies of the organic substance in the Bat-Bayos sediments of Dagestan. More than 400 samples representing 16 boreholes and natural exposures in the five districts surveyed were examined.

On the whole, the Dagestan Bat-Bayos sediments are characteristically low in organic substance, with an average of 0.643% organic carbon* (the organic carbon Clarke for sediments is about 1%). However, the known Dagestan sediments may be regarded as somewhat enriched in organic carbon with respect to the average organic carbon content of Jurassic sediments (0.43%) as cited by P. D. Trask [7].

As indicated by studies, the content of organic carbon in these sediments depends upon the lithologic composition of the rocks. Sandstones

*Organic carbon was determined volumetrically.

tain the smallest amounts of organic carbon; the higher the clay content of the rock, the higher is its organic carbon content. In the three rock types we have differentiated, clays, aleurolites, sandstones, organic carbon decreases in the following sequence: clays to aleurolites to sandstones (Table 1). The same trends have been reported by many other investigators, although our materials were different from ours [7, 8, 9, 10].

Our studies confirmed previously established relationships. As shown by M. Strakhov [9], the relationship between the organic carbon content and granulometric compo-

Table 1

Rock	Number of Analyses	% C _{org.}
Clays	230	1.09
Aleurolites	134	0.66
Sandstones	64	0.181

sition of the rocks is governed by the law of mechanical differentiation. V. V. Veber [11], proceeding from his studies of modern analogues of oiliferous facies, concluded that organic material may be accumulated in sandy sediments under certain conditions in quantities sufficient for its subsequent transformation into bitumen. This conclusion leads to certain doubts, however, as was pointed out correctly by M. F. Mirchink [11]. Accumulations of organic substance in sandstones are possible in some natural environments under certain definite conditions, but so far nothing is known about the scale or extent of such accumulations. In any case, the available data do not justify conclusions to the effect that the accumulation of organic material in sandstones is sufficiently great for its subsequent transformation into bitumen. There is enough evidence, on the other hand, on the accumulation of organic material in clays for us to regard these as oleogenic rocks [8, 12, 13].

The tendency of several investigators to set certain definite limits on the organic content of clays that would identify them as oleogenic rocks [8, 13] can hardly be regarded as justifiable. It is this consideration that helps us explain the fact that different investigators propose different limits for the organic carbon content of clays that would qualify them as oleogenic. These limits differ from district to district and also depend on the age of the sediments. Thus, according to V. D. Arkhangel'skiy, the organic carbon content of oleogenic rocks should not be lower than 2%, while this limit is 1.5 to 2% according to V. V. Vassoevich [13]. Z. L. Maymin [14] indicates 0.5% organic carbon as the order of magnitude for Devonian oleogenic rocks in the Kara-Ural Region. We are dealing, therefore, with a wide range of variations in the organic carbon content of oleogenic rocks, from 0.5 to 2%.

It is evident that oleogenic clayey sediments contain different quantities of organic material in different geologic environments. Consequently, it is not the absolute content of organic substance but

the degree of enrichment, with respect to organic substance, as again its content in the overlying and in the underlying suites, that must be taken into account in the recognition of oleogenic clays in every case.

The results of our determinations of organic carbon in sediments from exposures and boreholes are presented in Tables 2 and 3. As

Table 2. Organic Carbon Content of Bat-Bayos Sediments, Dagestan (Boreholes)

District	Clays					Aleurolites			
	Borehole	No. of analyses	Min.	Max.	Av.	No. of analyses	Min.	Max.	Av.
				% Corg.				% Corg.	
Ogni	48	10	0.707	10.750	2.300	2	0.171	1.650	0.4
Khosh-Menzil	27	2	1.830	2.700	2.260	6	0.040	1.740	0.4
Duzlak	13	3	1.835	2.000	1.930	4	0.694	2.385	1.7
Berekey	20	15	0.405	2.470	1.229	2	0.743	1.630	1.1
Eldama	1	3	0.328	1.305	0.819	10	0.002	1.440	0.4
Range and Average	-	-	0.328	10.750	1.307	-	0.002	2.385	0.4

District	Sandstones					All Rocks	
	Borehole	No. of analyses	Min.	Max.	Av.	No. of analyses	Av.
				% Corg.			% Corg.
Ogni	48	5	0.043	0.654	0.257	17	1.155
Khosh-Menzil	27	1	0.178	0.178	0.178	8	1.06
Duzlak	13	5	0	0.184	0.066	12	1.236
Berekey	20	14	0	0.765	0.247	31	0.887
Eldama	1	-	-	-	-	13	0.650
Range and Average	-	-	0	0.765	0.187	-	0.776

shown in these tables, there is a variation in the content of organic carbon in samples from exposures and boreholes. On the whole, the borehole samples contain more organic carbon than the samples representing natural exposures. If the organic carbon content of the exposures averages about 0.509%, the average for the borehole sample is 0.776%.

As shown by our studies, the extent of weathering of the organic material depends on the lithologic composition of the rock. Such weathering is insignificant in sandstones but is quantitatively appreciable in clays. Aleurolites occupy the intermediate position.

Thus, the % Corg. in sandstones from exposures is 0.174, as against 0.187 in sandstones from the boreholes. This relationship is not quite the same in clays. Clays from the exposures and from the boreholes contain, on the average 0.872% and 1.307% Corg., respectively.

Examination of the trends in the Corg. content in the profile of the Bat-Bayos sediments of Dagestan indicates a variation in quantities of organic material accumulated in the sediments with time depending on the rate of the accumulation. For example, the organic carbon varied from 0.328 to 10.75% in clays from the districts under reconnaissance. Sandy-aleurolitic rocks show similar relationships.

Table 3. Organic Carbon Content of Bat-Bayos Sediments, Daghestan Exposures

Lith.	Clays				Alcalimines			
	No. of analyses	Min.	Max.	Av.	No. of analyses	Min.	Max.	Av.
			% Corg.				% Corg.	
clay - brown	11	0.106	1.361	0.771	4	0.270	0.522	0.476
clay - Kal.	8	0.683	1.367	1.094	-	-	-	-
clay	15	0.368	1.049	0.691	1	0.344	0.344	0.344
clay - Clay	11	0.331	3.80	1.700	4	0.133	1.575	0.699
clay	8	0.106	1.689	0.641	7	0.168	1.620	0.390
clay	12	0.169	1.309	0.372	3	0.294	0.297	0.297
clay	11	1.816	1.056	1.877	1	0.225	0.225	0.225
clay	19	0.315	1.820	1.080	8	0.119	1.405	0.630
clay	26	1.081	1.832	0.381	17	0.104	1.856	0.460
clay - Clay	5	0.335	1.439	1.080	1	0.225	0.225	0.225
clay - Clay	14	0.772	3.520	1.362	3	0.301	1.120	0.609
clay	5	0.652	1.186	0.869	6	0.012	0.901	0.542
clay	10	0.169	0.850	0.811	12	0.020	0.915	0.481
clay	17	0.490	1.520	0.368	17	0.042	1.135	0.489
clay	24	0.215	1.201	0.636	20	0.118	1.258	0.529
clay	8	0.021	1.090	0.486	6	0	0.447	0.227
clay and average	-	0.021	3.520	0.872	-	0	1.620	0.481

Lith.	Sandstones				All Rocks	
	No. of analyses	Min.	Max.	Av.	No. of analyses	Av.
			% Corg.			% Corg.
clay - brown	3	0.056	0.156	0.250	20	0.590
clay - Kal.	1	0.068	0.068	0.068	9	0.581
clay	3	0.097	0.093	0.097	19	0.404
clay - Clay	-	-	-	-	15	1.199
clay	-	-	-	-	16	0.965
clay	2	0.070	0.085	0.077	17	0.302
clay	2	0.172	0.353	0.262	14	0.467
clay	-	-	-	-	27	0.355
clay	3	0.0066	0.067	0.045	36	0.296
clay - Clay	-	-	-	-	8	0.632
clay - Clay	-	-	-	-	10	0.368
clay	5	0.158	0.403	0.268	16	0.599
clay	3	0.061	0.064	0.223	25	0.475
clay	7	0.062	0.689	0.240	41	0.532
clay	3	0.113	0.514	0.243	47	0.471
clay	8	0	0.273	0.111	22	0.241
clay and average	-	0	1.589	0.174	-	1.599

The regional content of organic carbon of the sediments investigated is likewise subject to considerable variation. The range for the natural sediments is 0.241% (Apskh.) to 1.199% (Rubas-Chay); the range for the sediments under reconnaissance is 0.650% (Eldama, Borehole 1) to 0.241% (Duzlak, Borehole 13).

Such marked variations in the content of organic carbon in different profiles may be explained by differences in the physico-chemical environments of the sedimentation, in different parts of the basin, at the time of the deposition of the Bat-Bayos materials.

The data indicate a measure of impoverishment of the sediments with respect to organic carbon toward the shores of the Middle Jurassic Basin as well as in places where the sediments are generally thin. This is probably caused by aeration of bottom waters in the shallow parts of the basin.

In characterizing organic material, it is essential to ascertain not only the quantitative aspects of the problem but also the qualitative ones, that is, the proportions of different fractions of the organic substance. By fractions we mean bitumen, humic acids, and the insoluble organic materials.

Total organic carbon in the rock is an indicator of the total organic substance. The coefficient of the conversion of organic carbon to organic substance is generally taken as 1.6 [7].

Table 4 presents the average relationships of the organic material in borehole samples. Organic material of the Bat-Bayos rocks is represented chiefly by the insoluble fraction; bitumen constitutes a much smaller part of the total organic substance, and humic acids are absent.

Table 4

District	Borehole No.	No. of analyses	CLAYS					
			% of Rock			% of Organic Substance		
			Org. subst.	Bitumen	Humic acids	Insol. residue	Bitumen	Humic acids
Ogni	48	10	3.68	0.426	0	88.43	11.57	0
Khosh-Menzil	27	2	3.62	0.0825	0	97.74	2.26	0
Duzlak	13	3	3.09	0.236	0	92.36	7.64	0
Berekey	20	15	2.57	0.144	0	94.36	5.64	0
Eldama	1	3	1.31	0.148	0	88.71	11.29	0
Average	-	-	2.10	0.207	0	90.14	9.86	0
District	Borehole No.	No. of analyses	ALEUROLITES					
			Org. subst.	Bitumen	Humic acids	Insol. residue	Bitumen	Humic acids
			Org. subst.	Bitumen	Humic acids	Insol. residue	Bitumen	Humic acids
Ogni	48	2	1.46	0.09	0	94.11	5.89	0
Khosh-Menzil	27	6	1.408	0.07	0	95.04	4.96	0
Duzlak	13	4	2.74	0.272	0	90.07	9.93	0
Berekey	20	2	1.90	0.08	0	95.77	4.23	0
Eldama	1	10	0.768	0.119	0	84.55	15.45	0
Average	-	-	1.652	0.125	0	90.60	7.80	0
District	Borehole No.	No. of analyses	SANDSTONES					
			Org. subst.	Bitumen	Humic acids	Insol. residue	Bitumen	Humic acids
			Org. subst.	Bitumen	Humic acids	Insol. residue	Bitumen	Humic acids
Ogni	48	5	0.416	0.136	0	67.62	32.38	0
Khosh-Menzil	27	1	0.288	0.02	0	93.14	6.86	0
Duzlak	13	5	0.106	0.069	0	32.27	62.73	0
Berekey	20	14	0.40	0.09	0	77.5	22.5	0
Eldama	1	-	-	-	-	-	-	-
Average	-	-	0.299	0.078	0	73.99	26.01	0

The relative prominence of bitumen in the balance of the organic substance depends on the type of the rock. Bitumen in sandstones varies from 6.86 to 62.73% of the total organic substance (Borehole 27, Ash-Menzil and Borehole 13, Duzlak, respectively), with an average of 16.01%. The proportion of bitumen in the organic substance of aleurolites and clays is much lower (Table 4).

The bitumen content decreases from sandstones to aleurolites and in aleurolites to clays. This may be explained by the fact that bitumen in clays has a syngenetic character, while bitumen in sandstones is of a secondary origin and is derived by migration from clays.

The relationships indicated in this study constitute one of the proofs of the source-rock theory of oleogenesis which involves the formation of oil and gas deposits by migration and accumulation of the bitumens originally dispersed in the source rock.

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RELATIVE ABUNDANCE OF RUBIDIUM IN
GRANITES OF THE USSR*L. I. Sazhina*

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Abstract

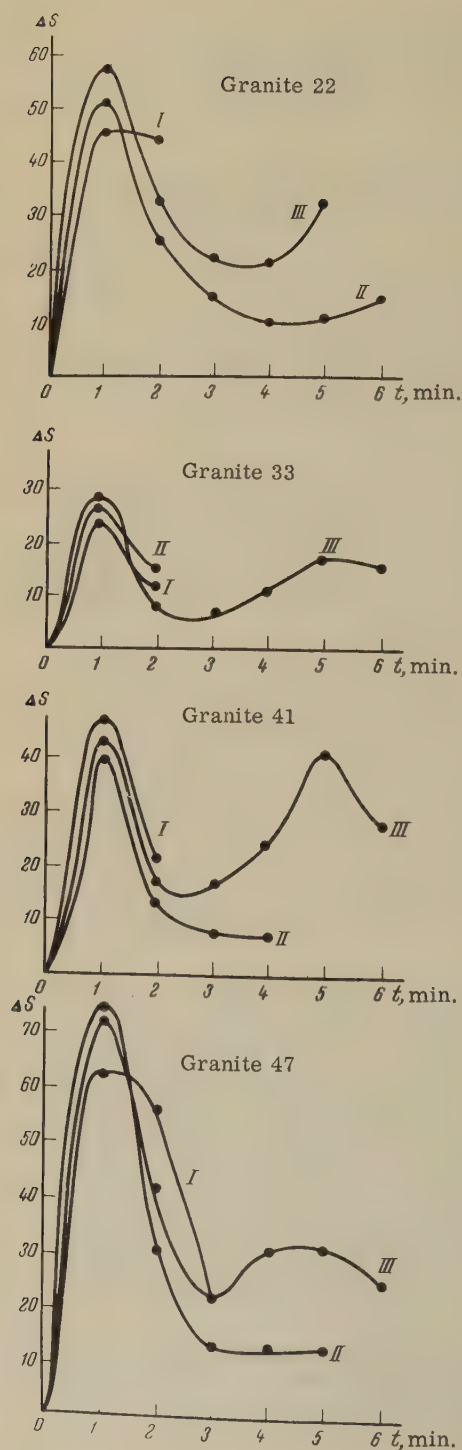
Quantitative determinations of the rubidium content in granites from various parts of the Soviet Union (90 samples) show that average rubidium content in the granites is 0.0257%.

In order to ascertain the relative abundance of rubidium in granitic gneisses of the Soviet Union, we examined spectrographically 90 samples of granites collected by the staff of the Institute of Mineralogy and Crystal Chemistry, Academy of Sciences of the USSR, in different parts of the country (Ukraine, Karelia, Ural, Yenisei Range, Eastern Transbaikalia, Eastern Sayan, Primorye, and Kolyma).

The analytical work was done under the direction of N. V. Lizunov, Chief of the Spectrographic Division, IMGRE AN SSSR.* The analysis was by the three-standard method, with measurement of the absolute density of the rubidium line, $\lambda = 7800\text{\AA}$. The source of the radiation was an AC activated arc, with generator of the DG-1 type and the current of 10 to 12a. A 20 milligram aliquot of the sample was placed in a cavity of a carbon electrode (diameter of the cavity: 4 mm; height: 7 mm) previously filled with powdered carbon. This latter device made it possible for us to keep track of the volume of the test material in the carbon and to distribute it at a uniform distance from the surface of the electrode.

The upper electrode was sharpened to a wedge in order to restrain the arc from wandering over the electrode surface. By means of a spherical illuminating lens, the central part of the arc was projected onto the slit of a "Fuess" glass monochromator with the chamber with a 7 cm cassette. The spectrum was photographed on "Infra 760" film. Density of the line was determined by MF-2 microphotometer on a logarithmic scale. The range of concentrations here studied was from 0.003 to 0.3%. Reproducibility of the results was ± 10 to 20%. There were variations in potassium and sodium content of the granites and it was necessary, for that reason, on some cases, to employ corrections, in order to minimize the effects of the major constituents on

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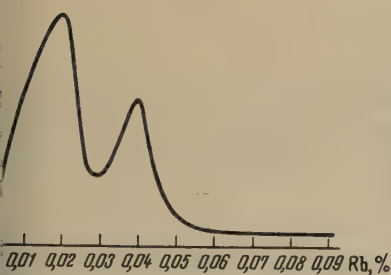


the density of the lines and, at times, to increase sensitivity of the determination. NaCl [1] was generally used as a diluting agent in the determinations of lithium, rubidium, and cesium. In the analysis of granites, however, it developed that sodium sulfate, Na_2SO_4 , was more effective than NaCl, as a diluent.

Three types of spectrographic analysis involving (a) volatilization of undiluted granite, (b) volatilization of granite diluted with NaCl, and (c) volatilization of granite diluted with Na_2SO_4 , enabled us to ascertain to some extent, the character of the volatilization and excitation of rubidium.

The density curves of the rubidium line have two peaks in the presence of Na_2SO_4 . The effects of Na_2SO_4 and NaCl on rubidium are about the same during the first two minutes of combustion in the arc; the two curves practically coincide and their peaks are of the same height. At the fourth minute, however, a second peak develops in line III (Fig. 1) and the total density of the line becomes greater than when NaCl was used as a diluent of the sample. T. F. Borovik-Romanova [2] reported a similar increase in the density of the lithium line in the presence of Na_2SO_4 , in the analysis of anhydrites (CaSO_4).

Fig. 1. Effects of dilution with NaCl and Na_2SO_4 on volatilization of rubidium from sample. ΔS —difference between densities of the rubidium line and the background; t —time allowed for the volatilization; I—granite without additions; II—granite with added NaCl (1:1); III—granite with added Na_2SO_4 .



2. Frequency distribution of the granites analyses depending on their rubidium content.

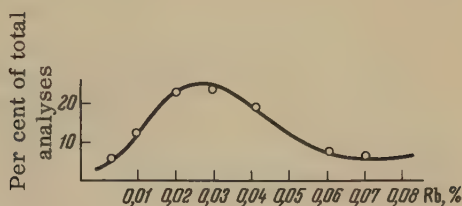
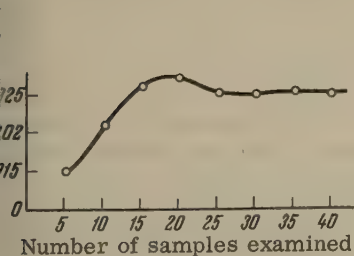


Fig. 3. Frequency distribution of muscovite and two-mica granites analyses depending on their rubidium content.

We examined five types of granites: biotitic, plagioclase, 2-mica muscovite, alkali, and aplitic. Inasmuch as biotitic granites represent the bulk of granite of the earth's crust, we gave most of our attention to this type in the selection of our test materials. The rubidium content of our biotite granites ranged from 0.003 to 0.09%, with most of the analyses falling between 0.01 and 0.05% (Fig. 2). In the case of 2-mica and muscovite granites, the rubidium range was from 0.003 to 0.077% and most of the analyses were within 0.01 to 0.04% (Fig. 3).

The representative character of our data on biotite granites is illustrated by Figure 4, which shows definitely that 25 analyses are sufficient for a reliable determination of the average rubidium content of these granites.

The rubidium averages for the 2-mica and muscovite, the alkali, and the aplitic types of granites are naturally less representative. However, taking into consideration the subordinate role of these varieties, in comparison with the biotite type, as well as the narrow range of the variation in their rubidium content, it appears feasible to make use of these findings in deriving the rubidium average for granites of



4. Frequency distribution of average rubidium in biotite granites depending on number of samples examined.

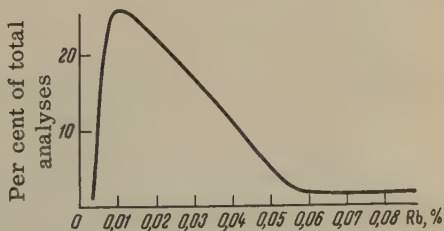


Fig. 5. Frequency distribution of samples of the USSR granites examined depending on their rubidium content.

Table 1

Type of granite	Number of samples from principal regions of the USSR	Per cent Rubidium	
		Range of Variation	Average
Biotite	54	0.003 to 0.09	0.025
Two-mica and muscovite	21	0.003 to 0.077	0.031
Alkali	6	0.01 to 0.041	0.031
Aplite-like	6	0.0087 to 0.044	0.018
Plagiogranites	3	0.007 to 0.012	0.009
Total	90	0.003 to 0.09	0.025

the USSR. We calculated accordingly the rubidium averages for different types of granites, on the basis of the foregoing results (Table 1).

As indicated by the analyses (Fig. 5), the largest number of determinations falls within the 0.01 to 0.05% range which serves to define the rubidium average for the USSR granites, namely, 0.025%.

According to available data [3], the average rubidium content of acidic rocks in different districts varies from 0.01 to 0.05%. Our results are very close to the findings by foreign investigators, for acidic rocks, in 1955, namely: Butler: $3 \times 10^{-2}\%$; Smales: $2.3 \times 10^{-2}\%$; Herzog and Pinson: $2.2 \times 10^{-2}\%$. Finally, Ahrens, in one of his recent studies, reports that his results in 1952-1954 ($5 \times 10^{-2}\%$) proved to be twice as high as the true [5].

Our rubidium averages for the USSR granites, therefore, are in close agreement with the most recent results for different regions of the earth's crust.

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THE CHARACTER OF THE ASSOCIATION OF GERMANIUM WITH ORGANIC CONSTITUENTS OF COAL

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Abstract

The complex of chemical elements being sorbed in the coal was separated by the method of electrodialysis. Germanium was not found in the products of electrodialysis. The conclusion is that germanium is present in coals in the form of metal-organic compounds.

That germanium is associated with the organic constituents of coals has been proved by numerous investigators. This association is expressed in the enrichment of the lighter fractions of the organic matter with respect to germanium [1, 2] and in the dependence of the germanium content of the coal on the amounts of petrographic constituents of the vitrinite group [3,4]. There are differences in the opinions, however, with regard to the character of this association. Some investigators believe that germanium is present in coal in a sorbed form [2,5], while others presume the existence of organic compounds of germanium. We have carried out, in this connection, studies of a group of chemical elements known to be sorbed by coal. This group of elements was isolated from the coal by electrodialysis. A certain part of this group may be present in coals in the form of soluble minerals.

An enrichment of germanium in the lighter fractions has been definitely proved by our studies of coals from the Kizelov Basin. The dependence of germanium on vitrinites is illustrated by Figs. 1 and 2. We have reason to believe, therefore, that the Kizelov coals are no different from coals of other basins with regard to the nature of their germano-germanium associations.

We performed eight electrodialysis experiments with coals of the Kizelov Basin containing 1 to 9 grams of germanium per ton. Ten-gram aliquots of the samples were first finely ground in water and then placed into a 3-chamber electrodialyzer. The volume of the electrolyte was 180 to 200 cm³, the potential gradient was 18 volts per cm and the diaphragms were cellophane and leather. Electrodialysis was carried out for 24 to 36 hours after which anolytes and catholytes were evaporated to dryness and the residues were analyzed qualitatively spectrographically.

The sum of the dialysed ions was about 10 milliequivalents per 100 grams of coal. The following elements were detected in the anolyte and the catholyte: beryllium, sodium, magnesium, aluminum, silicon, phosphorus, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, potassium, strontium, yttrium, tin, barium, ytterbium, lead, and bismuth. Germanium, however, was not detected among the elements whose association with coal is due either completely or partially due to sorption.

All of the elements here enumerated which were liberated from the sorption complex were also detected in the coal ash. We have reason, therefore, to believe that all of these elements are present in coal as sorption-bound complexes and as water-soluble and water-insoluble compounds, including metal-organic ones.

The reliability of our results was tested on a sample of a brown coal from one of the coal fields of the USSR kindly placed at our disposal by V. M. Ratynskiy. This sample contained more than 100 g. of germanium per ton. The sample was dialyzed for 15 hours and the sum of the ions liberated by the dialysis was about 31 milliequivalents per 100 g. coal; i. e., three times as high as in the coals from the Kizelov Basin. However, no germanium could be isolated by dialysis even from this coal.

Electrodialysis of coal ash obtained by the low-temperature combustion of the previously dialyzed aliquots of coal led to

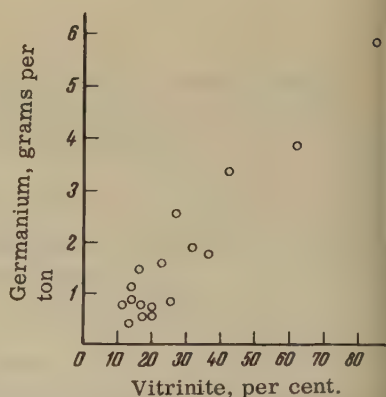


Fig. 1. Dependence of germanium content on quantity of vitrinite in coal of the Kizelov Basin.

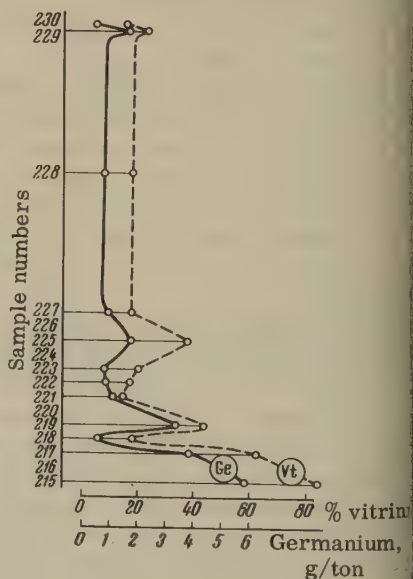


Fig. 2. Variations in content of germanium and vitrinite in reference to thickness of coal horizon (Horizon 13, Mine No. 24/38, Kizelov Basin).

ation of the germanium in the anode chamber. Inasmuch as we know germanium is liberated on the anode [6] during the electrodialysis aqueous germanium dioxide, it appears reasonable to assume that germanium is present as the dioxide in the ash of the coal which was separated from the sorbed elements by the previous electrodialysis.

Our findings indicate the absence of germanium in the sorption complex of coal, and we are led to the conclusion that germanium is more strongly bound to the organic substance than it could be by sorption. The binding in question is probably chemical, as an organic compound of germanium.

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THE AGE OF CERTAIN RARE-METAL GRANITIC INTRUSIONS IN CENTRAL KAZAKHSTAN

G. N. Shcherba and A. I. Ivanov

DISCUSSION

An article by L. V. Komlev and co-workers was published in Proceedings of the Sixth Session of the Committee on the Absolute Age of Geologic Formations and in *Geokhimiya*, No. 8, 1957, in which the majority view of the geologists as to the post-Harz age of the rare-metal granitic intrusions in Central Kazakhstan was definitely disproved, on the premises of a series of age determinations by the helium-argon, and the lead methods.

L. V. Komlev, S. I. Danilevich, *et al.*, in affirming a late Caledonian origin (Devonian) of the ore-bearing intrusions, make the following statement in their recent article: "A substantial modification must be introduced also into the patterns of metallogeny, to the extent that the greatest manifestations of the rare-metal mineralization must be regarded now as derivatives of a late Caledonian and not of the late Harz intrusive complex." [2, p. 654.]

This conclusion was reached by the authors on the basis of their analyses of samples of granites and of their derivatives from Akchatau, Meytas, and Zhanet. These districts were examined by us in detail. We also made some supplementary determinations of absolute age in the instance of the Zhanet and the Akchatau. Let us now attempt to consider our findings in reference to the reasonably firmly established geologic interrelations.

THE AKCHATAU MATERIALS

The host rocks of the Akchatau intrusions are Silurian sandstones and shales overlain unconformably by effusive-pyroclastic complexes of dacitic composition whose age is believed to be Devonian, although, to some other geologists, the age is Lower Carboniferous, which is more probable. Both of these structural tiers are identifiable by their faulting but only in the district and not in the mineralized area itself. The extensive areal distribution of these monotonous shales, sandstones, and the overlying effusives, over tens of thousands of square kilometers, and the direct extension of their structures into the mineralized part of the district leave no doubt as to their belonging to the same respective age groups.

Table 1. Sequence of Intrusive Complexes in the Akchatau District

Rocks	Forms	Relation to host rocks
Microdiorites	Stocks	Cut through sandstones and shales
Adamellites of SE Massif	Narrow, elongated	Cut through sandstones, shales, microdiorites, and the overlying effusives
Leucocratic granites of Main Massif	Slightly elongated, multiphase	Cut through all of the preceding rocks and contain the rare-metal mineralization

The sequence of the intrusive activities in the Akchatau is shown in Table 1.

Our conclusions [6] had found an additional confirmation in 1956, when mineralized leucocratic granites piercing the overlying adamellites of the Main Massif were discovered by borings at depths exceeding 200 meters.

Thus the lower age limit of the later intrusion is considerably younger than the Devonian, younger even than the Lower Carboniferous, i.e., prior to its emergence, there was a folding of the effusives followed by the intrusion of the adamellites. It is for these latter granites and for the associated ore veins, regarded as late Harz in age, that L. V. Komlev, K. K. Zhironov, *et al.*, [1, 2], who determined their age by different methods (helium for monazites; lead for monazite and brannerite; argon for biotite), give the absolute age from 270 to 338 million years [2, p. 651] or 300 to 317 million years on the average. The relatively good agreement of the results obtained by different methods and the extensive use of the lead method (so highly reliable, as a rule), make such findings quite convincing at first glance, although, as a matter of fact, they *definitely contradict the geologic data* (if we accept the absolute age scale which is accepted by L. V. Komlev and co-workers). L. I. Ivanov and N. I. Zamyatin of the IGEM Kaz. SSR* Laboratory performed many repeated determinations of the age of granite, apatite, and biotite from the very latest massif of the leucocratic ore-bearing granites, by the argon method, and found it to be 240 to 260 million years.

METHODS

Argon was determined by the volumetric method, in two parallel calculations of the Khlopin-Gerling type, by procedures given in the literature [7, 8, 9]. The argon content of every sample was

determined two or three times, in different aliquots and in different installations. The average relative error of the determination, on the whole, did not exceed 5%.

The determinations were carried out by the rapid dipicryl amine method. The results were corrected for the argon in the air. In calculations of the age, the λ_k was taken as 6.02×10^{-11} years and λ_β as 4.9×10^{-10} years. These data are in a closer harmony with the firmly established geologic relationships and they confirm the late Harz age of the intrusions, even though they still seem to be somewhat too high.

DATA ON THE ZHANET

A gently sloping apron of a geosynclinal fold formed of Lower Carboniferous effusives and tuffs of a dacitic and liparatic composition was intruded by a succession of granodiorites, granophyre granites, and, finally, by leucocratic ore-bearing granites. This sequence is close to the previously described one, for the Akchatau, and was established on the basis of the detailed studies by R. N. Malkova, V. P. Muravev, and V. L. Melnikova and was confirmed subsequently by borings and by mining reconnaissance.

Pegmatites, greisen, quartz-feldspar ore-bearing veinlets, and alteration of the host rocks (feldspathization) are associated with the later granitic intrusion which is analogous to the Akchatau intrusion in its composition.

L. V. Komlev, S. I. Danilevich, and others had estimated the age of the monazites from the Zhanet greisen at 320 million years, by the ratio of total lead to uranium and thorium; i.e., as Upper Silurian to Lower Devonian (*sic*). The age of monazites was determined by the helium method and the age of granites, feldspars from pegmatites, and muscovites from greisen, by the argon method at the Laboratory of Geologic Sciences, Academy of Sciences of Kazakh SSR. The results are shown in Table 2.

As may be seen in Table 2, the age of the Zhanet granites is close to the age of the Akchatau granites and is also in agreement with the geologic data. Here too we must remark that the age results are rather too high, since, by certain geologic considerations, the age data for muscovite and monazite (Permian) are closer to the true age than the age indicated by the feldspar. In this case, too, there exists a

Table 2. Data on Age of Materials from the Late Granites of Zhanet

Sample	Age, Million Years
Feldspar from pegmatite	243
Muscovite from greisen	215
Monazite	207

tantial discrepancy between our data and that of L. V. Komlev who published the age in question at 320 million years.

CONCLUSIONS

We cannot accept the assertions by L. V. Komlev, S. I. Danilevich, E. Ivanova, and others to the effect that "our findings are incontrovertible in regard to the absolute age of the Akchatau, while our preliminary findings for the Maytas and the Zhanet indicative of a 290 to 300 million years age for the rare-metal-bearing intrusions serve completely to undermine the ideas of their 'Permian' or 'late Harz' granites" [2, p. 653.] Such a conclusion is by no means "incontrovertible," inasmuch as, in this particular case, the very same granites which our authors call Devonian cut through the already folded paleozoically identified sediments not only of Devonian but also of Lower Carboniferous age. Such conclusions may be drawn only by closing one's eyes to geology, by ignoring the available data on the true relationships of the rocks. Premature conclusions of this sort are conducive only to confusion.

Having presented the age pattern of the magmatic complexes of Central Kazakhstan in their Table 3 [2, p. 654], the authors had lost sight of the fact that the terminal complexes II of the Harz Epoch, 250 to 300 million years old, are the very same granites to which they assigned the age of 300 to 320 million years.

Granites of an analogous petrochemical composition containing tungsten ores were proved in the extensive areas of Central Kazakhstan and Altai and were described by many investigators. The recent publications of V. K. Monich, E. V. Shevchenko, G. D. Shcherba [3, 4], present data to the effect that the Akchatau intrusions (the Kalbaitan, the Gornyi Altai Complexes) cut through the dislocated sediments of the Lower Carboniferous and even of the Middle Carboniferous and are younger than these sediments accordingly. The late Harz granites of the Akchatau Complex in other districts of the Central Kazakhstan (Baynazar, Batystau, Karaoba) is confirmed also by our determinations of their absolute age by the argon and by the helium methods. The data cited by us come even closer to the true relationship between the intrusive complexes here discussed, although even these calculations tend toward too high results (*i.e.*, indicate a greater age) in the case of the younger granites, even as high as the Upper to Middle Carboniferous.

L. V. Komlev thinks that the age figures he has obtained are "incontrovertible," it should be desirable, in this particular case, to solve the problem of a fundamental revision of the absolute age scale, but he accepts the relatively closely agreeing scales of Holmes, S. A. F. M., and the VSEGEI.* As to the geologic relationships, it is for a

period of tens of years, by this time, that geologists have been finding only confirmations of the previously accepted sequence of the magmatisms. The age of the younger granites in the Akchatau Complex has not fallen below the Middle Carboniferous in any one of the districts so far examined; it is only the upper boundary of the age that is still obscure, although, in any event, there are no reliable indications that the intrusions cut through the Mesozoic sediments.

We are faced, therefore, with the necessity of a critical analysis of the empirical data on absolute age and of ascertaining, prior to their publication, the reasons why they do not agree with the facts observed in nature. It is clear that we must continue to accumulate materials for further refinements of the absolute geologic scale, by the data obtained for our country.

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CHRONICLE

The All-Union Conference on Geochemical and Radiometric
Methods of Prospecting and Exploration of Oil and
Gas Deposits

(April 21-26, 1958)

A conference on geochemical methods of prospecting and exploration of deposits of oil and gas was held in Moscow, April 21-26, 1958. The conference was organized by the Academy of Sciences of the USSR, at the request of the Gostekhnika, as a special meeting for a discussion of the problem with the participation of the interested ministries. Approximately 240 delegates of 68 organizations attended the conference. They represented the Academy of Sciences and its different branches, Academies of Sciences of the Member-Republics, several institutions of higher learning, several institutes and industrial agencies of the Ministry of Geology and Conservation of the USSR, the plans of the USSR and of the RSFSR, The National Scientific-Technological Committee of the Council of Ministers of the USSR, central sovnarkhozes, and other agencies. Together with the Soviet geologists, scientists from German Democratic Republic, Czechoslovakia, Poland, Rumania, and Yugoslavia participated actively in the conference.

The conference was opened with the introductory address by Academician D. I. Shcherbakov, Academic Secretary of the Division of Geologic and Geographic Sciences. Twenty basic reports were presented at the conference; 68 Soviet specialists took part in the brief communications and in the discussions. Moreover, 7 reports and communications were presented by foreign scientists.

A. A. Saukov's report was on the migration of chemical elements and the theoretical basis of geochemical methods of prospecting for oil and gas deposits. The report dealt especially with the characteristics of the migrations in solid, liquid, and gaseous phases and with the spectroscopic methods of metallometric, hydrochemical, biogeochemical, and geophysical surveys based on the migration of chemical elements, including examples of their application.

A. A. Sokolov's report has shed some light on the scientific premises of geochemical prospecting and exploration for oil and gas, showing that abyssal gases at oil and gas deposits are strikingly different from the gases of surficial origins in their concentrations of the C_2-C_4 hydrocarbons which is diagnostic of oil and is useful accordingly in prospecting for oil and gas by geochemical methods.

Principles of microbiological prospecting methods were discussed in the report by S. I. Kuznetsov, who demonstrated the abundance of

hydrocarbon-oxidizing bacteria over economic deposits of oil and gas and the absence of such bacteria in non-petroliferous districts. The growth of methane-oxidizing or of propane-oxidizing bacteria may take place at the minimum of 0.001% and 0.01% concentrations of these two gases respectively.

The F. A. Alekseev's report was on the subject of the theoretical basis of radiometric methods of exploration for oil and gas, on the well-known premises—the presence of radiometric anomalies (the too-low gamma-fields) over deposits of oil and gas.

In his report on the "Movement of Deep Underground Waters," A. I. Silin-Bekchurin presented evidence to the effect that there is a lateral movement of underground waters at great depths below the surface in many parts of the world, including the Russian Platform, North Africa, India, etc., and that petroliferous areas may be also enveloped by such movement, which must be taken into account in the problems of origin as well as of dissipation of petroleum deposits.

The report by A. B. Ronov was devoted to the distribution of organic carbon in sedimentary rocks of the Russian Platform. The author showed that deposits of petroleum are associated with stratigraphic complexes regionally enriched with organic carbon and that this relationship needs be considered in large-scale appraisals of economic possibilities in petroliferous areas.

Methods and techniques of prospecting for oil and gas deposits were topics of the following reports: G. A. Mogilevskii's "The Present State of The Problem of Gaseous and Bacterial Anomalies and the Rational Methods of Their Identification," E. A. Bars's "Hydrochemical Investigations in Prospecting for Oil and Gas," V. A. Kovda's and P. S. Slavin's "Soil Geochemical Indications of Oil," V. N. Florovskii's "The Luminescent-Bituminologic Method of Study and Prospecting for Oil and Gas Deposits," V. A. Sokolov's "The Gas-Analytical Procedures and Apparatus and Ways in Which they are to be Improved."

Some very interesting data were presented in the reviews by B. P. Yasenev entitled "The Results and the Effectiveness of the Gas Surveys in the USSR" and by Yu. M. Yurovskii, "The Progress of Gas Logging in the USSR." Specifically, they showed that out of the 142 gas anomalies discovered in different folded areas in the USSR, in new areas, 80% (or 60% of the total) proved to be positive, by means of exploratory drilling in depth. Gas logging proved to be even more effective, to the extent of 70%.

As the result of broad discussions of the reports, the conference adopted a resolution on the importance of geochemical and radiometric methods of the exploration pertinent to the attainment of the objective set by the Party and the Government: to raise the output of petroleum up to 350-400 million tons, within the next 15 years, and to raise the output of natural gas up to 270-320 billion cubic meters per year.

The research and the field work on record had proved that there is a large-scale migration of oil and gas in nature causing development of anomalies in rocks and in underground waters. Discovery and

pretation of such anomalies are the objectives of geochemical and radiometric methods of exploration. It has been proved in practice that gasometric, geochemical, (emission) logging, and microbiological surveys had yielded correct prognoses, in many instances, which were subsequently validated by discoveries of new deposits of coal and oil.

Alongside the unquestionable successes in the development of theoretical premises and of practical applications of the methods, the conference had noted a number of defects in the organization of such studies: the studies are scattered and uncoordinated; some of their theoretical aspects are poorly developed; the instrumentation in the discovery of the anomalies needs further refinements, etc.

The conference recommended certain measures, in order further to develop and to improve geochemical and radiometric methods and further to expand their applications in the field, including creation of a special coordinating committee at the Division of Geologic and Graphical Sciences of the Academy of Sciences of the USSR, with participation of representatives of the Ministry of Geology and Conservation of the USSR, the USSR Gosplan, and the National Scientific-Technological Committee of the Council of Ministers of the USSR.

A. A. Saukov

THE TENTH CONGRESS OF MINING ENGINEERS AND METALLURGISTS AT THE FREIBERG MINING ACADEMY

The regular Congress of Mining Engineers and Metallurgists was held in Freiberg (German Democratic Republic) May 28-31, 1958, under sponsorship of the Freiberg Mining Academy—one of the oldest mining academies in the world, founded in 1765. This Congress acquired an international significance because of some 1800 attending guests—delegates from other German cities, including 200 scientists and specialists from Western Germany (FRG), and representatives of many European and Asiatic countries.

A special address by Prof. E. Sadetzky-Kardos on "The Rare Elements and Geochemistry" was a dedication to geologic studies at the plenary session of the Congress. Prof. E. Sadetzky-Kardos gave a detailed characterization of the new methods of geochemical research in the relative abundance and distribution of rare elements and of the isotopes, emphasizing their importance in the theory of the formation of ores, geo-energetics, and the progress of modern technology.

Among the many reports presented at the geologic sessions, there were "On the Asymmetric Development of Orogenic Factors" by Prof. E. Kraus (München), and "On the Age of Regional Metamorphism of Western Alps" by Prof. E. Bederke (Göttingen) who documented the multi-stage character of the ancient metamorphism and of rock alterations related to successions of periodic tectonic adjustments.

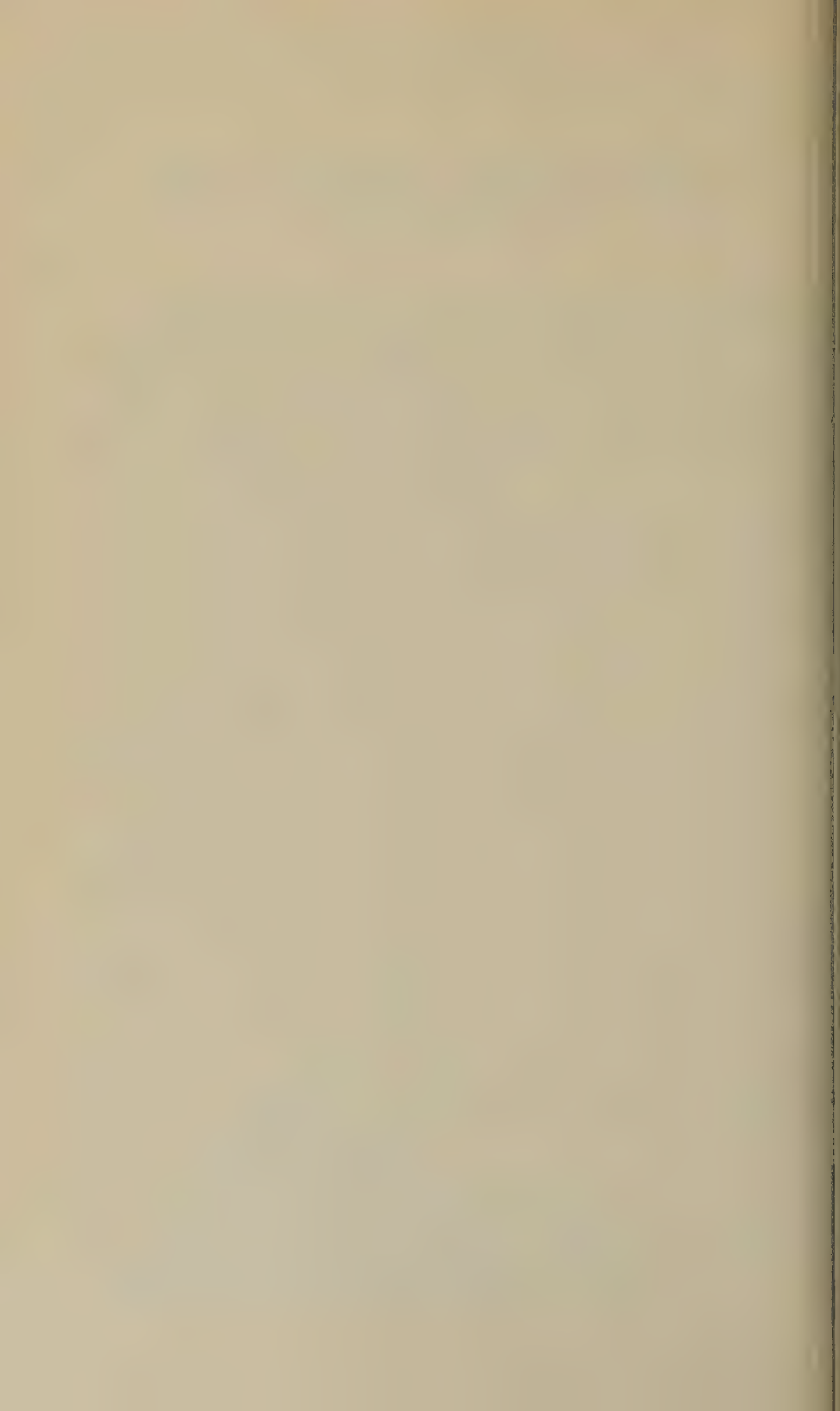
There was considerable interest in the paper by Prof. Dmitrov (Sofia, Bulgaria), "On the Metamorphic Complexes of Bulgaria," who emphasized the development of the Precambrian in the crystalline base of the Rhodope Mountains and of the Devonian metamorphic complexes in the base of the Harz structures; and by Prof. V. Marmo (Otoniemi, Finland), "Granites and Formation of Ores," who rejected a direct relationship of ores to granites and proved that the spatial proximity of intrusions to ores is due to tectonic factors, in most instances.

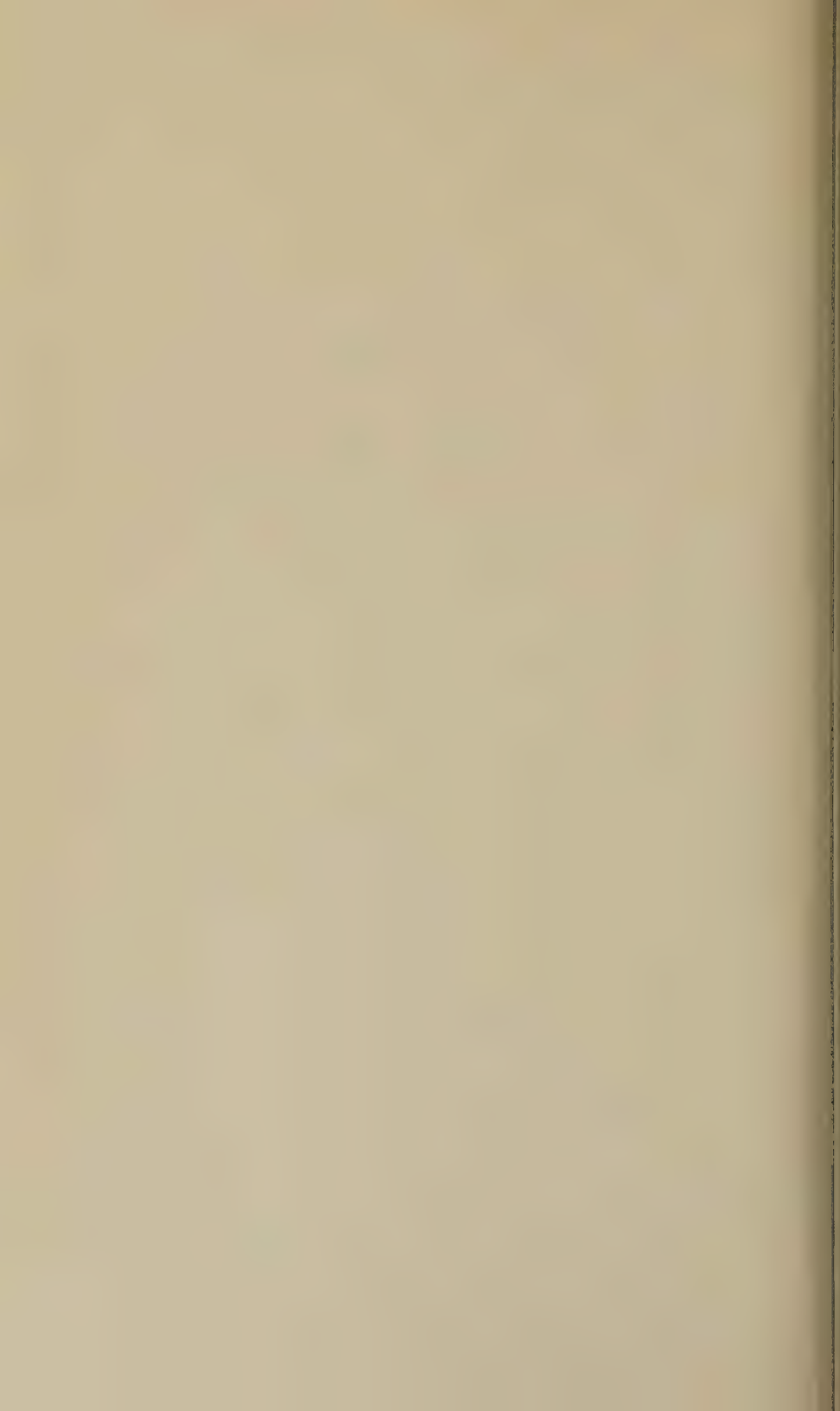
The paper by Prof. Schril (Harz) also attracted attention of the participants of the sessions, in its presentation of very interesting observations on re-deposition of ores from Harz deposits in the overlying Mesozoic sediments, in Alpine time, with illustrations drawn from several mineralized districts.

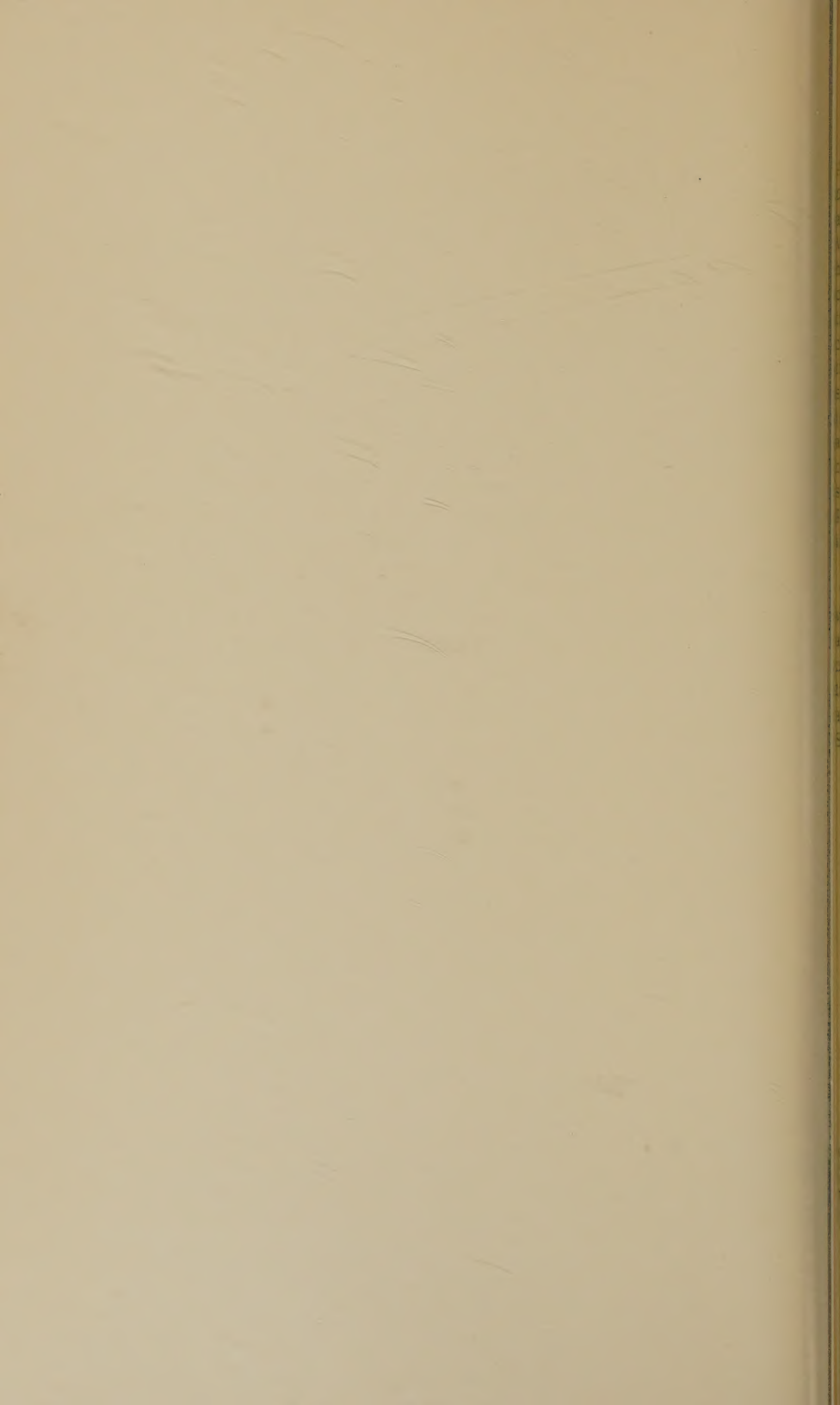
The report by A. P. Vinogradov, A. I. Tugarinov, V. V. Zhirovaya, S. I. Zykov, K. G. Knorre, and V. I. Lebedev on "The Age of Granites and Ores of Saxony," with its data on the absolute age as shown by radioactive methods, was received with a high degree of interest resulting in lively discussion and exchange of opinions.

There were several geologic trips during the Congress.

A. I. Tugarinov







Geokhimiya began publication in 1956 under the able editorship of P. Vinogradov. It is the Soviet counterpart of *Geochimica et Cosmochimica Acta*, having practically identical fields of interest and covering and publishing approximately the same number of pages per year. With the great increase in geochemical research in the U.S.S.R., there have come into being a variety of highly specialized journals in geochemistry and related fields. It is probably better to begin translating the more general journal first and follow with some of the more specialized ones if interest appears to justify this course of action and if financial arrangements can be made. It is hoped that there will be sufficient interest in this journal to justify translation and publication (of complete volumes) of the issues for 1957 and 1958. If individuals or organizations who would purchase such translations will write to one of the Editors, the work will be undertaken when enough expressions of interest have been received to justify the expense involved. Expenses presumably would be approximately the same as for the 1958 issues.

The National Science Foundation has been most cooperative in this venture. They not only indicated willingness to back it financially but also helped in calculating probable costs and possible subscription income during the first year. It is on these figures, and those for advertising and administration, that the grant is based. It is a pleasure to acknowledge here the advice, assistance and support of the National Science Foundation.

Earl Ingerson
Translation Editor

In matters of subscription for *Geokhimiya* refer to: Moskva K-104, Pushchinskaya, 23, Akademkniga. Chief Editor: A. P. Vinogradov. Editorial Council: V. I. Baranov, K. A. Vlasov, V. I. Gerasimovskii, D. S. Korzhinskii, A. Saukov, N. I. Khitrov (Responsible Secretary), V. V. Scherbina (Deputy Chief Editor).

Geochemical News is an informal bi-monthly newsletter published by the Geochemical Society and sent without charge to all of its members. It contains news of the activities of the Society, such as summaries of Council Meetings, reports of committees and plans for the future. It also includes announcements of forthcoming meetings and symposia of interest to geochemists, personalia, announcements or short reviews of books of geochemical interest, information on translations and translation services, letters and short notes by members, etc.

During 1959 the *Geochemical News* will contain a series of articles on research in geochemistry in laboratories in the United States, not only those associated with universities but industrial laboratories as well.

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Geochimica et Cosmochimica Acta is the official journal of the Geochemical Society. It is an international journal interested in the broad aspects of geochemistry, both geographically and subject-wise; articles have been received from contributors from all of the (inhabited) continents.

New chemical data and interpretations involving chemical principles are emphasized. For example, papers in chemical mineralogy, petrology, oceanography and volcanology are acceptable, as are those in the chemistry of meteorites, whereas it would be suggested that those in descriptive mineralogy and volcanology, petrography, physical and biological oceanography and physical meteorites, be sent to other journals specializing in these subjects.

Thus, the subject coverage is closely similar to that of *Geokhimiya*. Also, the number of pages published per year is of the same order of magnitude. Subscription prices are as follows:

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